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Biodiesel from vegetable oils

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ABSTRACT

Biodiesel is gaining acceptance in the market as fuel and lubricant. It is expected that biodiesel industries will rapidly grow worldwide in the coming years and information on biodiesel feedstock, production, and characteristics will be crucial than ever especially for those using vegetable oils as feedstock as these are currently the major sources for making biodiesel. In the present paper, a comprehensive review is reported on feedstock, production technologies, and characteristics of biodiesel. More specifically, selected available vegetable oils are explored as feedstock for biodiesel production. Production technologies including latest catalyst developments are discussed. Finally, biodiesel characteristics and parameters influencing the corresponding properties are revealed. Since this paper covers a wide range in biodiesel area, it serves as a general public education medium as well as a research reference for biodiesel production from vegetable oils.

Contents

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1. Introduction

The depleting trend of conventional, non-renewable, fossil-based fuel has triggered research and development on alternative renewable energy. Biodiesel is one of the most promising renewable energy in this century. Recently, a 5.54 fossil energy ratio (FER) was reported [1] which means one unit of fossil energy input is required to produce 5.54 units of biodiesel energy output. This FER shows a stunning energy return of biodiesel that surpasses other fuels [2]. Furthermore, FER of biodiesel is expected to be increased even further in the coming years mainly due to increased crop yield, adoption of energy-saving farm practices, and continuous development of energy-efficiency technologies. In addition, biodiesel has many superior properties as compared to petroleum diesel such as lower exhaust emissions, biodegradable, non-toxic, renewable, and free of sulfur [3–5]. Since biodiesel is renewable and environmentally friendly, the use of this fuel is a shift towards sustainable energy.

The history of biodiesel is as long as that of diesel engine itself. The use of vegetable oils was investigated as early as the era when diesel engine was developed. Rudolf Diesel (1858–1913), the inventor of diesel engine, tested peanut oil as fuel for his engine. Many vegetable oils were investigated during "historic times" which includes palm oil, soybean oil, cottonseed oil, castor oil, etc. These early publications showed satisfactory performance of vegetable oil as fuel for diesel engine [6]. However, there were concerns that their higher costs as compared to petroleum fuel would prevent their prevalent uses. In spite of their performance in diesel engine, vegetable oils create engine problems when used as diesel fuel especially in direct-injection engines. The major drawback of vegetable oils is their high viscosity which causes coking and trumpet formation on the injectors resulting in poor atomization and ultimately leads to operational problems such as engine deposits [7]. Four possible solutions to reduce viscosity of vegetable oil were proposed: transesterification, pyrolysis, dilution with petroleum-based fuel, and emulsification [8]. Transesterification is the most common method which yields mono alkyl esters of long chain fatty acids or fatty acid alkyl ester (FAAE). This idea was originated back in 1938 that the glycerin part has no calorific value and is likely to cause excess carbon deposit on the engine and therefore should be eliminated from the vegetable oils. The engine should run on the residue fatty acid [9]. The residue fatty acid is what is today known as "biodiesel", although ester was not mentioned during that period. In fact, the glycerol part in triglyceride molecule is responsible for the high viscosity of vegetable oil, whereas the fatty acid part is 10 times less viscous than vegetable oil. During the summer of 1938, an urban bus running between Brussels and Louvain was operated on ethyl ester from palm oil. The engine performance was satisfactory and there was a report on a significant decrease in viscosity of ethyl ester as compared to that of vegetable oil. The term "biodiesel" made its first appearance in a paper published in 1988 and this term was used exponentially thereafter [6].

Biodiesel is mono alkyl esters of long chain fatty acids that can be prepared from acyl-glycerol (usually triglyceride) in vegetable oils via transesterification with short chain alcohols. The use of biodiesel is simple yet effective as it is miscible with petroleum based diesel in all proportions and can be used as fuel either in pure biodiesel or blended with petroleum based diesel fuel [10]. The blends of biodiesel and petrodiesel are often coded such as B20, which indicates the blend of 20 vol% biodiesel and 80 vol% petrodiesel. This paper will discuss details on feedstock (vegetable oils), transesterification, and biodiesel characteristics.

2. Feedstock

The feedstock for biodiesel production can be categorized as lipid feedstock and alcohol feedstock. The lipid feedstock includes vegetable oils, animal fats, and, more recently, other plant-like organisms such as micro algae and cyanobacteria. This paper focuses on vegetable oils as lipid feedstock. The vegetable oils used as lipid feedstock for biodiesel production highly depend on regional climate that is rapeseed oil in European countries and Canada, soybean oil in United States, and palm oil in tropical countries such as Indonesia and Malaysia. Coconut oil is another lipid feedstock used for synthesis of biodiesel in coastal areas. Potential non-edible oils used as lipid feedstock in India include jatropha oil (*Jatropha curcas*) and karanja oil (*Pongamia pinnata*) [11]. Table 1 summarizes oilseed price and availability which are important parameters to consider as biodiesel feedstock. Soybean oil dominates the world oilseed production while rapeseed production is second only to soybean oil. The oil content in soybean and rapeseed is 21% and 35%, respectively. Despite the lesser availability, palm oil is an interesting source for biodiesel production due to its lower price and relatively high oil content (40%). This oil also gives highest oil yield per area per year as compared to other oils.

Oilseeds contain droplets of lipid which can be extracted as vegetable oils. The major component of vegetable oils is triacylglycerol (TAG) or triglyceride (TG) which is a molecule composed of three esters of fatty acid chain (acyl group) attached to the

Table 1
World oilseed production, average oil price and oil content of various oilseeds.

Plant	Oil content (%)	Oilseed production[a] (Million metric tons)	Average oilseed price[a] (U.S.D/metric ton)	Average oil price[a] (U.S.D/metric ton)	Yield (kg/ha/yr)	Reference
Rapeseed	35	46.72	375	852[b]	600–1000	[12–14]
Soybean	21	235.77	254	684	300–450	[12,13,15]
Sunflower seed	44–51	30.15	n/a	n/a	280–700	[12,13,16]
Palm	40	10.27	n/a	655	2500–4000	[12–14]
Cottonseed	18	46.02	n/a	787	n/a	[12,14]
Peanut	36–56	32.36	395	1253	340–440	[12,13,17]
Copra	65–68	5.28	537	n/a	n/a	[12,18]
Coconut	63	n/a	n/a	812	600–1500	[12–14]

[a] Data in 2006/2007.
[b] Canola oil.

Table 2
Molecular structure of triglyceride, diglyceride, and monoglyceride.

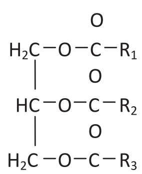
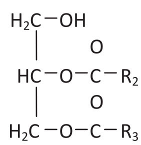
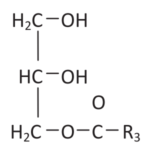
Triglyceride	Diglyceride	Monoglyceride
		

Table 3
Structures of common fatty acids found in vegetable oils.

System name	Common name	Symbol	Formular	Double bond position[a]
Saturated				
Decanoic	Capric	C10:0	$C_{10}H_{20}O_2$	–
Dodecanoic	Lauric	C12:0	$C_{12}H_{24}O_2$	–
Tetradecanoic	Myristic	C14:0	$C_{14}H_{28}O_2$	–
Hexadecanoic	Palmitic	C16:0	$C_{16}H_{32}O_2$	–
Octadecanoic	Stearic	C18:0	$C_{18}H_{36}O_2$	–
Eicosanoic	Arachidic	C20:0	$C_{20}H_{40}O_2$	–
Docosanoic	Behenic	C22:0	$C_{22}H_{44}O_2$	–
Tetracosanoic	Lignoceric	C24:0	$C_{24}H_{48}O_2$	–
Monounsaturated				
Hexadecenoic	Palmitoleic	C16:1	$C_{16}H_{30}O_2$	9c
Octadecenoic	Petroselinic	C18:1	$C_{18}H_{34}O_2$	6c
Octadecenoic	Oleic	C18:1	$C_{18}H_{34}O_2$	9c
Octadecenoic	Elaidic	C18:1	$C_{18}H_{34}O_2$	9t
Octadecenoic	Vaccenic	C18:1	$C_{18}H_{34}O_2$	11c
Eicosenoic		C20:1	$C_{20}H_{38}O_2$	5c
Eicosenoic	Gadoleic	C20:1	$C_{20}H_{38}O_2$	9c
Eicosenoic	Gondoic	C20:1	$C_{20}H_{38}O_2$	11c
Docosenoic	Erucic	C22:1	$C_{22}H_{42}O_2$	13c
Polyunsaturated				
Hexadecadienoic		C16:2	$C_{16}H_{28}O_2$	
Octadecadienoic	Linoleic	C18:2	$C_{18}H_{32}O_2$	9c12c
Octadecatrienoic	Linolenic-α	C18:3	$C_{18}H_{30}O_2$	9c12c15c
Octadecatrienoic	Linolenic-γ	C18:3	$C_{18}H_{30}O_2$	6c9c12c
Octadecatrienoic	Eleostearic	C18:3	$C_{18}H_{30}O_2$	9c11t13t
Octadecatrienoic	Calendic	C18:3	$C_{18}H_{30}O_2$	8t10t12c

[a] *c*=*cis* formation; *t*=*trans* formation.

glycerol backbone (glycerol group). When one and two acyl groups are replaced by hydroxyl groups (–OH), it is called diacylglycerol (DAG) or diglyceride (DG) and monoaclyglycerol (MAG) or monoglyceride (MG), respectively. Acylglycerol is a term referred to TAG, DAG, or MAG and is depicted in Table 2. The fatty acid chains usually range from 10 to 24 carbon atoms. In saturated fatty acids, all carbon atoms are attached to hydrogen, oxygen and carbon and there is no double bond between carbon atoms. When a pair of hydrogen is removed from a fatty acid chain, one double bond is present in it and therefore termed as monounsaturated fatty acid. Further removal of hydrogen leads to a presence of two or more double bonds and it is called polyunsaturated fatty acids. These fatty acids are frequently represented by a symbol such as C18:1, which indicates a fraction consisting of 18 carbon atoms and one double bond. Typical fatty acids attached to TAG found in vegetable oils are presented in Table 3. Configurational isomers of unsaturated fatty acids can be arranged in *cis* and *trans* orientations. Naturally occurring fatty acids in vegetable oils have *cis*-formation whereas the unnatural *trans*-isomers occur due to partial hydrogenation process. The Latin prefixed *cis* and *trans* describe the orientation of hydrogen atoms attached to carbon atoms at position next to the double bond. In *cis*-isomer, hydrogen atoms are attached on the same side causing "V" shape of the fatty acid chain. On the other hand, when two hydrogen atoms are attached on the other side of each other, *trans*-isomer is formed and the molecular structure is linear. The shape of configuration determines "stacking" of TAG molecules, proximity between molecules, and intermolecular forces between molecules. All these factors are key parameters for determining properties of various vegetable oils such as crystallization and melting temperature.

The major difference between various vegetable oils is the type of fatty acids attached in the triglyceride molecule. Fatty acid compositions of various vegetable oils are shown in Table 4. Fatty acid composition is of utmost importance as it determines fuel properties of biodiesel derived from corresponding vegetable oils [38]. Fatty acid composition also determines degree of saturation/unsaturation and molecular weight of vegetable oils. The degree of saturation/unsaturation and molecular weight of vegetable oils can be calculated by iodine value and saponification value, respectively. Higher iodine value and saponification value indicates higher degree of unsaturation and lower molecular weight of the corresponding vegetable oils. Iodine and saponification values of selected vegetable oils are shown in Table 5 [39].

2.1. Soybean oil

"Soybean" or "Soya" is referred to *Glycine max* which is found only under cultivation and is a member of the Papilionaceae [40]. The origin of soybean is not clear, for the genus *Glycine* has two major gene centers; eastern Africa and Australia. It is believed that the genus *Glycine* was dispersed from Australia to the whole Pacific region including China via migratory birds as seeds carriers. Based on historical and geographical evidence, north eastern China has been considered as the region of origin of soybean domestication. There are a number of cultivated soybean derived products during historic time such as various liquids prepared from soybean and soybean curd known as "tofu". From China, soybean spread through nearby countries such as Korea, Japan, and Southeast Asia

Table 4
Fatty acid compositions of vegetable oils.

Vegetable oils		Fatty acid composition (wt%)											Reference
Common name	Species	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:0	22:1	
Canola	*Brassica campestris*	–	–	3.1	0.2	1.3	56.6	22.4	14.0	0.4	0.2	0.1	[19]
Canola	*Brassica napus*	–	–	4.3	0.3	1.7	61.0	20.8	9.3	0.6	0.3	–	[19]
Black mustard	*Brassica nigra*	–	1.5	5.3	0.2	1.3	11.7	16.9	2.5	9.2	0.4	41.0	[20]
Oriental mustard	*Brassica juncea*	–	–	2.3	0.2	1.0	8.9	16.0	11.8	0.8	5.7	43.3	[21]
Brown mustard	*Brassica juncea*	–	–	2.2	0.2	1.2	17.4	20.5	14.1	0.7	0.5	28.1	[22]
Wild mustard	*Brassica juncea*	–	0.1	2.6	0.2	0.9	7.8	14.2	13.0	0.8	1.5	45.7	[23]
White mustard	*Sinapis alba*	–	–	3.1	0.2	0.7	9.1	11.7	12.5	0.7	–	46.5	[22]
White mustard	*Sinapis alba*	–	0.1	2.8	0.2	1.1	25.0	11.6	8.6	0.7	0.6	32.8	[24]
Abyssinian mustard	*Brassica carinata*	–	–	3.1	–	1.0	9.7	16.8	16.6	0.7	–	42.5	[25]
Soybean	*Glycine max*	–	–	10.1	–	4.3	22.3	53.7	8.1	–	–	–	[26]
Soybean	*GMO*[a,b]	–	–	3.5	0.1	2.8	22.7	60.3	9.8	0.2	0.2	–	[27]
Soybean	*GMO*[a,c]	–	0.1	10.9	0.1	5.7	27.5	51.5	3.0	0.5	0.4	–	[27]
Soybean	*GMO*[a,d]	–	0.1	23.8	0.7	3.8	15.4	44.1	11.0	0.4	0.6	–	[27]
Soybean	*GMO*[a,e]	–	–	8.0	0.1	24.7	17.2	39.2	8.3	1.5	0.7	–	[27]
Palm	*Elaeis guineensis*	0.3	1.2	44.3	–	4.3	39.3	10.0	–	–	–	–	[28]
Palm	*Elaeis oleifera*	–	0.2	18.7	1.6	0.9	56.1	21.1	–	–	–	–	[28]
Palm kernel	*Elaeis guineensis*	50.1	15.4	7.3	–	1.8	14.5	2.4	–	–	–	–	[28]
Palm kernel	*Elaeis oleifera*	29.3	25.7	10.1	–	1.8	26.4	4.5	–	–	–	–	[28]
Palm kernel	*Aiphanes acanthophylla*	41.5	20.5	10.2	–	3.4	15.8	7.4	–	–	–	–	[29]
Palm kernel	*Buttia capitata*	39.2	6.4	4.2	–	3.0	11.9	3.5	–	–	–	–	[29]
Palm olein[f]		0.3	1.2	40.6	0.2	4.3	41.9	11.9	0.4	0.4	–	–	[30]
Palm stearin[f]		0.3	1.5	61.1	0.1	4.8	25.8	6.5	0.4	0.5	–	–	[30]
Sunflower	*Helianthus annuus*	–	–	5.2	0.1	3.7	33.7	56.5	–	–	–	–	[26]
Sunflower	*GMO*[a,g]	–	–	3.1	0.1	1.5	91.5	2.1	–	0.2	0.7	0.1	[27]
Sunflower	*GMO*[a,g]	–	–	4.4	–	4.2	78.3	10.9	–	0.3	1.0	–	[31]
Sunflower	*GMO*[a,c]	–	0.1	7.5	0.1	1.9	13.3	76.0	0.1	0.1	0.4	–	[27]
Sufflower		–	0.1	6.4	–	2.3	11.6	79.3	–	0.3	–	–	[32]
Groundnut	*Arachis hypogea*	–	–	11.2	–	3.6	41.1	35.5	0.1	–	–	–	[26]
Corn	*Zea mays*	–	–	11.6	–	2.5	38.7	44.7	1.4	–	–	–	[26]
Olive	*Olea europea*	–	–	13.8	1.4	2.8	71.6	9.0	1.0	–	–	–	[26]
Olive (wild)	*Ximenia americana*	–	–	–	–	1.2	60.8	6.7	–	–	–	–	[33]
Cottonseed	*Gossypium hirsutum*	–	–	23.0	–	2.3	15.6	55.6	0.3	–	–	–	[26]
Linseed	*Linum usitatissimum*	–	–	5.6	–	3.2	17.7	15.7	57.8	–	–	–	[26]
Coconut	*Cocos nucifera*	50.9	21.1	9.5	–	4.9	8.4	0.6	–	–	–	–	[34]
Sesame	*Sesamum*	–	–	9.6	0.2	6.7	41.1	41.2	0.7	–	–	–	[26]
Rice bran	*Oryza sativa*	–	–	22.1	–	2.0	38.9	29.4	0.9	–	–	–	[35]
Jatropha	*Jatropha curcas*	–	–	18.5	–	2.3	49.0	29.7	–	–	–	–	[36]
Karanja[f]	*Pongamia glabra*	–	–	5.8	–	5.7	57.9	10.1	–	3.5	–	–	[33]
Karanja	*Pongamia Pinnata*	–	–	11.7	–	7.5	51.6	16.5	2.7	–	–	–	[37]
Neem[f]	*Azadirachta indica*	–	–	17.8	–	16.5	51.2	11.7	–	2.4	–	–	[33]
Sal[f]	*Shorea robusta*	–	–	6.2	–	43.0	41.3	2.1	–	5.5	–	–	[33]

[a] GMO=genetically modified oil.
[b] Low saturate.
[c] High linoleic.
[d] High palmitic.
[e] High stearic.
[f] Average value.
[g] High oleic.

Table 5
Iodine value and saponification value of vegetable oils.

Oil	Saponification value	Iodine value
Rapeseed, crude	179.0	109.9
Soybean, crude	190.7	134.6
Palm, crude	200.0	56.9
Palm kernel, crude	246.4	20.7
Sunflower, winterized	190.6	135.4
Sufflower, linoleic-rich, crude	190.3	143.6
Sufflower, oleic-rich, crude	189.3	93.2
Cottonseed, crude	195.2	105.0
Linseed, crude	189.6	188.0
Corn, soap stock	195.9	105.3
Rice bran, crude	180.1	103.9
Coconut, crude	256.4	9.9
Olive, refined	192.0	84.9
Sesame, crude	188.0	109.2

counties and finally around the world. Soybean was first mentioned in USA literature in 1804, exclusively used as a forage crop, and was not an important crop until the World War II, after which its production and economics in USA has grown exponentially. Today, soybean is the world's largest oilseed in terms of total production and international trades [41,42]. The oil content in soybean seed ranges from 15% to 22% depending on environmental conditions during seeds maturity. The major fatty acids are oleic (C18:1) and linoleic (C18:2) as can be seen in Table 4.

2.2. Rapeseed oil, mustard oil, and canola oil

The word "rape" is originated from latin word "rapum", which means turnip. This belongs to *Brassica* family including turnips, mustard, cabbage, rutabagas, broccoli, and kale [43]. Rapeseed crops were among the first crops domesticated in the early history.

It was used as source of cooking and illumination oil as early as 2000–1500 B.C. [44]. Due to its ability to tolerate low temperature, *Brassica* crops were among the few vegetable oil sources that could be cultivated in cold climate regions. The economically important crops in *Brassica* and *Sinapis* species include *Sinapis arvensis* (wild mustard), *Sinapis alba* (white mustard), *Brassica nigra* (black mustard), *Brassica carinata* (Abyssinian mustard), *Brassica juncea* (brown, oriental, and leaf mustard), *Brassica oleracea* (cabbage, kale, cauliflower, broccoli), *Brassica campestris* (turnip rape), and *Brassica napus* (rape, rutabaga) [45]. These seeds have oil content over 40% in which the dominant fatty acids include oleic acid (C18:1), linoleic acid (C18:2), and erucic acid (C22:1). When rapeseed has erucic content higher than 5%, it is called high erucic acid rapeseed (HEAR), while low erucic acid rapeseed (LEAR) is referred to rapeseed having erucic acid content less than 5%. Erucic acid contained in rapeseed should be avoided in daily dietaries. Many researchers reported that cardiac fat infiltration in experimental animals is caused by erucic acid present in HEAR and have thus concluded erucic acid as a toxic compound. This compound if fed in large quantities would result in heart lesions [43]. Although there is no evidence of adverse nutritional effects of erucic acid in humans, the research related to erucic acid in humans has not been studied as thoroughly as in experimental animals. The complexity of nutritional interactions between fatty acids intensifies difficulty in understanding the nutritional effect of erucic acid especially in the case of using humans as a test subject. The use of rapeseed oil containing high erucic acid level as edible oil has continuously been objected by many organizations throughout the history. The Canadian regulations state that in cooking oil, margarine, salad oil, simulated dairy product, shortening or food that resembles margarine or shortening, the erucic and cetoleic acid may not exceed 5% of the total fatty acid [46].

The pathway of biosynthesis of erucic acid involves the elongation of oleic acid. In brief, the erucic acid is the result of an addition of a two-carbon fragment to oleic acid to form eicosenoic acid (C20:1), followed by addition of another two-carbon fragment to eicosenoic acid to form erucic acid [46]. In the case of low erucic acid rapeseed (LEAR) such as *B. napus* (Canola Oil or Canadian Brassica), the genetic elongation ability of fatty acids is blocked, leading to the accumulation of the precursor fatty acid, i.e., oleic acid. The level of erucic acid can be genetically modified ranging from less than 1% to over 60%. A study showed a declining trend in erucic percentage in Canadian LEAR during 1980s [47]. The advent of low erucic acid rapeseed (LEAR) leads to a “phase out” of high erucic acid rapeseed (HEAR) from the food market, however, HEAR can be used in other industries such as fuel, lubricating oil, oleochemicals, and biopolymer production. In 1974, the so called “double-low” rapeseed, that is rapeseed low in erucic acid content and glucosinolate content, had become commercially available in Canada. Rapeseed crushers in Canada adopted the name “canola” as this “double low” rapeseed and canola oil dominated vegetable oils in Canadian diets. Under the Canadian Agricultural Products Standards (CAPS) Act, canola oil is defined as oil extracted from rapeseeds of *B. napus* L. and *B. campestris* L. species with low level in both erucic acid and glucosinolate content. The erucic acid content in canola oil shall not exceed 5% (w/w) [44,48].

2.3. Palm oil

The origin of palm is believed to be in Africa, but the most productive regions are located in Southeast Asia especially Malaysia and Indonesia, which together account for around 80% of the total world production. Palm first received its botanical name from Jacquin in 1763 as *Elaeis guineensis* [49]. The word *Elaeis* is derived from Greek word *elaion*, meaning oil, while *guineensis* implies its origin in Guinea coast. The genus *Elaeis* includes *E. guineensis* originated in Africa, *Elaeis oleifera* originated in Central and South America, and *Elaeis odora*, previously known as *Bercella odora*, which is not cultivated. *E. guineensis* is currently the main species planted commercially in Malaysia because it gives the highest yield per bunch while oil from *E. oleifera* is more unsaturated and this species gives less oil yield. The seed contains a shell and one, two, or three kernels. The kernel consists of layers of oily endosperm surrounded by a brown testa covered with a network of fibers. Palm is the most efficient oil-producing plant per area per year as can be seen in Table 1. There are generally two types of oil derived from palm including palm oil from mesocarp and palm kernel oil from kernel inside the seed [18,50]. Palm oil is more saturated than soybean oil and rapeseed oil as its major fatty acids include palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) as shown in Table 4. Palm kernel oil is more saturated than palm oil as it mainly contains lauric (C12:0), myristic (C14:0), and oleic (C18:1). Palm oil can be fractionated at ambient temperature (25–30 °C) into palm olein or oleic-rich oil (liquid fraction) and palm stearin or stearic-rich oil (solid fraction). Due to the saturated fatty acids contained in this oil, it has superior oxidation stability as compared to other vegetable oils.

2.4. Sunflower oil

The genus *Helianthus annuus* is a given botanical name for sunflower for which it is a member of Compositae of flowering plants growing throughout the world. The name stems from Greek word *helios* meaning sun and *anthos* meaning flower. Sunflower originated in Southwest United States and Maxico areas [42]. Sunflowers are cultivated most often for ornamental and sometimes for consumption. Sunflower seeds are edible and often crushed for oil extraction. The major fatty acids in sunflower oil are oleic (C18:1) and linoleic (C18:2). Sunflower is considered as one of the most ancient oilseed species as its cultivation can be traced back to 3000 B.C. Sunflower was once the world top-rank oil-producing plant prior to the advent of soybean boom after World War II.

2.5. Rice bran oil

Rice bran is the main source of rice oil. Lipid droplets can be extracted from rice bran using extruder, expander, and expeller to form a bran flake or pallet followed by solvent (usually hexane) extraction in an extraction bed. The majority of oil components are triacylglyceride (TAG) with palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) as major fatty acids. Diacylglyceride (DAG), monoacylglyceride (MAG), and sterols may be present in minor amounts. Rice bran oil is used widely in Asian countries due to its delicate flavor and odor. It is recently gaining interest as healthy oil since it reduces serum cholesterol [51].

2.6. Jatropha oil

Jatropha carcus is a member of Euphorbiaceae family. It originated in America but is harvested mainly in Asian countries especially in India. Jatropha is well adapted to arid and semi-arid conditions and it shreds its leaves in order to survive during drought seasons [51]. It can be grown on non-cultivated and degraded wasteland and therefore is considered as one of the most promising feedstock for biodiesel production [53]. Although Jatropha plant has low nutritional requirements, cultivation of Jatropha under acidic soil requires additional nutrients such as calcium and magnesium due to its preference for alkaline soil. Oil derived from Jatropha is non-edible due to curcin, a toxic compound, found in the seeds. Oil content ranges from 35% to 40% in

seed and 50% to 60% in kernel with oleic (C18:1) and linoleic (C18:2) as its major fatty acids.

2.7. Karanja oil

Karanja is a member of Leguminaceae family with *P. Pinnata* as its botanical name. It is an oil seed bearing tree native to humid and subtropical environments such as those in Philippines, Indonesia, Malaysia, Myanmar, Australia, India, and United States. It is highly tolerant to salinity and can be cultivated on degraded wasteland on a variety of soil types ranging from clay to sandy or stony. In addition, it plays an important role in improving soil quality so that the land exhausted of nutrients can be reused for agricultural purposes [52]. The oil droplets extracted from Karanja appear yellowish orange to brown and are not edible due to the presence of toxic flavonoids [54]. Oil content varies from 9% to 46% with oleic (C18:1) and linoleic (C18:2) as its major fatty acids.

2.8. Used cooking oil

Properties of used cooking oil depend highly on origin and history of the oil. The origin of used cooking oil determines fatty acid compositions while history or duration that oil exposed to heat, food, and oxygen during cooking determines the oil's physical and chemical properties such as viscosity, water content, free fatty acid content, and consists of polymerized and oxidized compounds.

Oil degradation during cooking occurs through 3 main reactions: thermolytic, oxidative, and hydrolytic reactions. In thermolytic reactions, the reaction occurs in absence of oxygen. High temperature is required to decompose saturated fatty acids to form alkanes, fatty acids, ketones, esters, diacylglycerides, etc. In addition, dimeric compounds appear to be the main derivatives as a result of thermolytic reactions of unsaturated fatty acids. Dimerization and polymerization of unsaturated fatty acids is reported to take place via Diel–Alder type reactions. For example, a reaction between conjugated diene from linoleate and oleate can take place to produce a tetra-substituted cyclohexane [55]. In the presence of oxygen, oxidative and nonoxidative reactions will occur simultaneously. Oxidative reactions occur in a series of initiation, propagation, and termination steps as shown in Fig. 1. The initial step involves an abstraction of hydrogen from unsaturated fatty acid to form free radical (R•) followed by an attack of molecular oxygen to these locations to form peroxide radicals (ROO•). The propagation phase involves intermolecular interactions, whereby the peroxide

Initiation:

$$RH \rightarrow R^{\bullet} + H^{+}$$

Propagation:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + H^{+} \rightarrow ROOH$$

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet}$$

Termination:

$$RO^{\bullet} + H^{+} \rightarrow ROH$$

$$OH^{\bullet} + H^{+} \rightarrow H_2O$$

Fig. 1. Scheme for oxidative reaction mechanism.

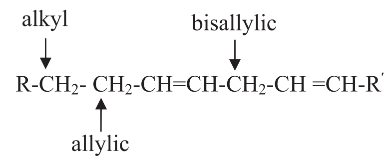


Fig. 2. Carbon–hydrogen bond positions in fatty acids.

radical abstracts hydrogen from an adjacent molecule, which gives rise to hydroperoxides (ROOH) and a new free radical. Carbon-hydrogen bond dissociation energies of fatty acid are lowest at biallylic followed by allylic positions (see Fig. 2). It is reported that lower bond energies for bisallylic and allylic hydrogens are 75 and 88 kcal/mol, respectively while those of methylene hydrogens are 100 kcal/mol [56]. As a result, hydrogens at bisallyic and allylic locations are favored site for abstraction by peroxide radical. Once formed, hydroperoxides tend to proceed toward further oxidation degradation leading to secondary oxidation derivatives such as aldehydes, acids, and other oxygenates [55]. Hydrolytic reactions take place between oil and water formed during food preparation. Formations of DAG, MAG, FFA, and glycerol are main derivatives from hydrolysis of TAG [57].

As a result of a combination of these reactions during food preparation, various reaction derivatives are formed leading to an increase in polar content of the oil. It is advised that used cooking oil should no longer be used for edible purposes when polar content exceeds 25% [58]. Therefore, used cooking oils were sold commercially as animal feed. However, in 2002, the European Union (EU) has enforced a ban on these waste oils as animal feed. It is because various harmful compounds are formed in used cooking oil during food preparation. When used cooking oil is mixed in feeding meals for domestic animals, these harmful compounds could return back into the food chain through animal meats [59]. This concern has raised interests in utilizing used cooking oil as feedstock for biodiesel production even further.

An obvious advantage of used cooking oil over other vegetable oils is its cheaper price. The prices of soybean, sunflower, yellow grease (FFA < 20 wt%), and brown grease (FFA > 20 wt%) are 18, 20, 9, and 5 to −5 cent/lb, respectively [60]. The negative value of brown grease price implies the cost associated with waste treatment prior to dumping. The availability of used cooking oil as a feedstock for biodiesel production is highly related to area population. Yellow grease generated in Canada is roughly equivalent to 4 kg production per person per year. Therefore, there would be approximately 124 kt of yellow grease produced annually in Canada [61]. As a comparison to used cooking oil, biodiesel produced from fresh vegetable oils would be more pricy. Zhang et al. [62] reported that on an average a $0.01/kg increase in canola seed cost would result in $0.03/kg increment in biodiesel price and the raw material cost is responsible for approximately 70–95% of biodiesel production cost when fresh vegetable oil is used as feedstock. Therefore, the use of used cooking oil for feedstock for biodiesel production attracts many biodiesel producers due to its economical benefits.

3. Biodiesel production

Transesterification is the most common method used to reduce viscosity of vegetable oils and produce biodiesel [7]. In addition to transesterification of TAG, biodiesel (FAAE) can be produced from free fatty acid (FFA) through esterification. Since ester is characterized by RCOOR group (R=alkyl group), TAG is a type of ester and the reaction that converts TAG into biodiesel is known as transesterification (transforming ester). In contrast, FFA is not an ester and therefore the reaction to produce biodiesel from FFA is called esterification (making ester). Transesterification is the reaction

between glycerides with short chain alcohols and it comprised of three consecutive reactions starting from TAG to DAG, DAG to MAG, and from MAG to glycerol (see Fig. 3). In each step, the reaction consumes one mole of alcohol and produces one mole of ester. In total, one mole of TAG reacts with three moles of alcohol to produce three moles of ester (biodiesel) and one mole of glycerol. In general, the reaction performance is influenced by various parameters such as type of alcohol, alcohol to oil molar ratio, FFA and water content, reaction temperature, reaction duration, and catalyst type. These parameters will be discussed in the following sections.

3.1. Effects of free fatty acid and water content

Free fatty acid and water content in the starting materials can significantly affect the ester yield and glyceride conversion in alkali-catalyzed transesterification process. All starting materials including lipid feedstock, alcohol, and catalyst should be substantially anhydrous. Prolonged contact with atmospheric air of alkali catalysts will reduce catalysts' efficacies through catalysts interaction with moisture and carbon dioxide in air. Also, it is critical that feedstock used in alkali-catalyzed transesterification should contain free fatty acid (FFA) less than 0.5 wt% [7]. The higher the acidity of oil, the lower is the conversion and yield in transesterification. If FFA is contained in the starting oil, extra alkali catalyst is needed to neutralize the FFA. The reaction between alkali catalyst and FFA would result in catalyst consumption as well as soap formation and water, and is referred to saponification (see Fig. 4a). Another example of saponification during transesterification is when water is present; it will favor hydrolysis of glycerides to form soap and glycerol (see Fig. 4b). In addition, water can promote hydrolysis of ester to form FFA, which lower the esters yield (see Fig. 4c). Soap formed during saponification causes increase in viscosity or gel formation which interferes with the transesterification reaction as well as glycerol separation [54]. Ma et al. [63] studied the effects of FFA and water on transesterification of beef tallow using sodium hydroxide and sodium methoxide as catalyst. It was reported that when 0.6% FFA was added, the yield of beef tallow methyl ester was minimal. Additional water present in the reaction mixture intensely diminishes the ester yield. They concluded that FFA and water content should be maintained below 0.5 and 0.06 wt%, respectively.

Low quality feedstocks such as used cooking oil are attractive due to their cheaper price. However, these feedstocks usually contain high amounts of FFA and water due to prolonged exposure to heat and contaminated moisture from food. Therefore, direct alkali-catalyzed transesterification of these oils is not applicable. Pre-treatment of these oils to remove FFA and water is usually required. Alkali refining is usually used in oil processing in order to remove FFA from oils [64]. In this process, 12% aqueous sodium hydroxide solution is required to neutralize FFA and to precipitate phosphatides. The treatment temperature and duration can be either 90 °C for few seconds (short-mix process) or 40 °C for 15 min (long-mix process). Then the oil-soap mixture is centrifuged to separate the aqueous phase containing water, soap, and precipitated phosphatides. The treated oil usually has FFA reduced to $<0.05\%$ and phosphorus to <2 ppm. The disadvantage of this process is the generation of waste water. In addition, FFA can be removed from vegetable oils through distillation [65]. The distillation temperature ranged from 100 to 180 °C. The distillation process should be performed under vacuum conditions in order to lower the operating temperature. If the operating temperature is too high, glycerides will degrade to generate more acids. This alternative is less preferred due to an additional cost associated with distillation step. Alternatively, a two-step acid-alkali esterification-transesterification process can be used [66]. In the first step, FFA is esterified with a short-chain alcohol with acid catalyst to produced ester. Since FFA was converted to ester in the first step, an alkali catalyst can be used in transesterification in the second step. A solid acid catalyst was also reported for simultaneous catalysis of esterification of FFA and transesterification of glycerides [67]. However, further research and development is required to improve conversion and ester yield.

3.2. Effects of alcohol used in transesterification

Stoichiometrically, one mole of TAG requires 3 mol of alcohol in transesterification. However, due to the reversible nature of the

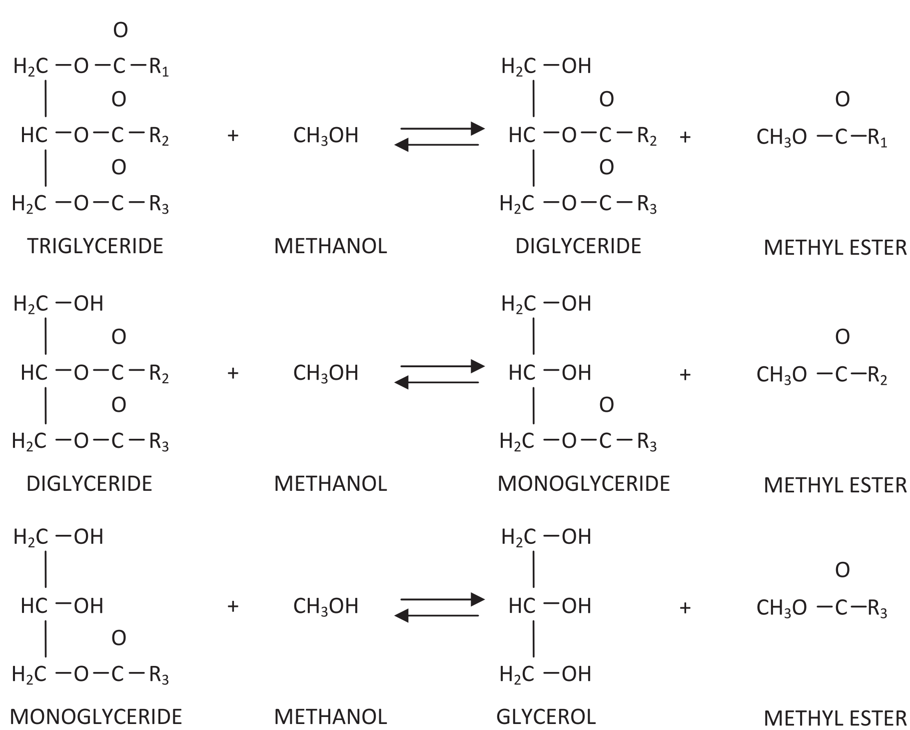


Fig. 3. Scheme for step-wise transesterification reaction.

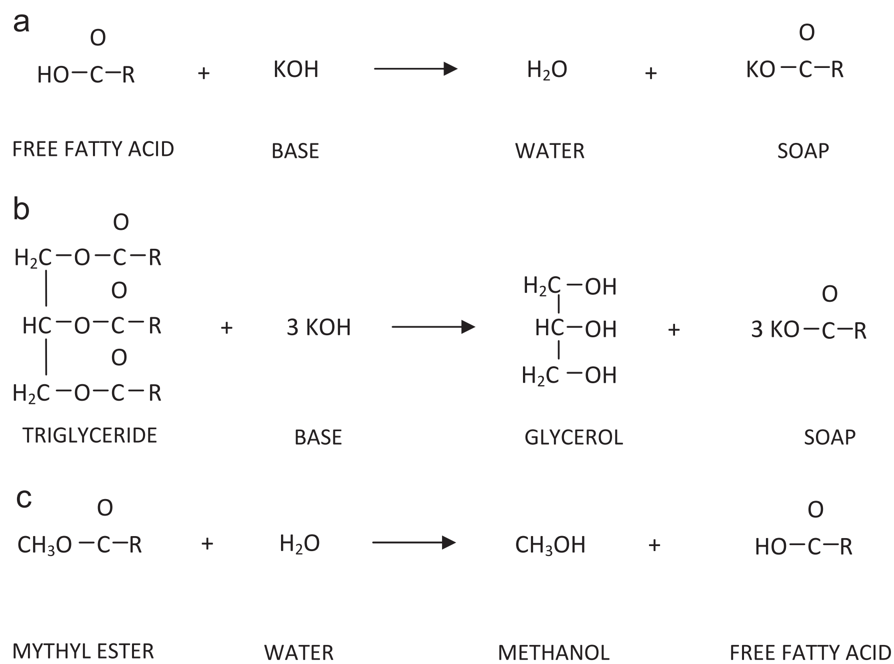


Fig. 4. Hydrolysis and saponification during transesterification (a) saponification of free fatty acid, (b) saponification of triacylglyceride and (c) hydrolysis of methyl ester.

reaction, excess alcohol is usually used in transesterification in order to shift the reaction to the product side. In general, 98% conversion can be achieved at 6:1 alcohol to oil ratio for an alkali-catalyzed reaction and an increase in alcohol used in the reaction does not increase conversion any further [68]. However, an optimum alcohol to oil ratio can be different depending on oil quality and type of vegetable oil used. It was reported that a maximum of 92% conversion was achieved using 10:1 methanol to oil ratio for biodiesel preparation from Karanja oil [69]. Leung and Guo [70] reported that 98% ester content can be obtained from transesterification of canola oil using 6:1 alcohol to oil ratio while transesterification of used cooking oil requires 7:1 alcohol to oil ratio to obtain 94% ester content. Transesterification of *Cynara cardunculus* L. oil requires 12:1 ethanol to oil ratio as an optimum ratio while an increase in ethanol to oil ratio to 15:1 decreases ester content [71]. Rashid and Anwar [72] also reported that further increase in alcohol used in transesterification of rapeseed oil beyond optimum ratio (6:1 in this case) would result in a reduction in ester yield. When too much alcohol is used in transesterification, the polarity of the reaction mixture is increased, thus increasing the solubility of glycerol back in to the ester phase and promoting the reverse reaction between glycerol and ester or glycerides thereby reducing the ester yield. Acid catalyzed reaction, however, requires higher alcohol to oil molar ratio (30:1) when compared to alkali-catalyzed reaction [73–75]. In some case, alcohol to oil ratio is increased up to 245:1 in order to obtain 99% conversion [76].

Type of alcohol used in transesterification can also affect the reaction performance. Methanol is most commonly used in transesterification mainly due to its economical benefit [7]. The disadvantages of using methanol are dependency on petroleum sources and low solubility of TAG in methanol. To illustrate the immiscible behavior of TAG in methanol, it is reported that a minimum mixing time of 3 min is required to sustain methanolysis of soybean oil [77]. The lag time of 2–3 min during methanolysis of soybean oil and sunflower oil is also reported [73,78]. This immiscibility behavior is often referred to as mass transfer resistance or mass transfer limitation which can be overcome by several methods including the use of rigorous mechanical stirring [79,80], an aid of co-solvent [81], the use of super critical conditions [82–84], and the use of other techniques such as microwave [85,86] and ultrasonic [87,88]. Attempts to improve the mass transfer of TAG have been made by using other alcohols such as ethanol, propanol, and butanol [89–91]. Biodiesel produced using bio-ethanol is completely renewable. The main disadvantage of ethanolysis is the lower reactivity of ethoxide. When alcohol reacts with homogeneous base catalysts, alkoxides which are the actual catalyst are formed. If ethanol is used instead of methanol, the carbon chain length is increased which leads to a decrease in nucleophilicity and consequently a reduction in reactivity of ethoxide as compared to methoxide [92]. It was found that when waste fryer grease is transesterified with a mixture of methanol and ethanol at equal molar ratio, the resulting biodiesel contains 50% more FAME than FAEE [66] which illustrates the higher reactivity of methoxide as compared to ethoxide. The lower polarity of ethanol has advantage and disadvantage on the transesterification process. On one hand, the lower polarity of ethanol alleviates the initial mass transfer resistance encountered in the case of methanolysis, hence increasing the initial rate of the reaction. On another hand, it improves mutual miscibility of ester and glycerol in which the catalyst resides and therefore promotes saponification. Therefore, in the case of ethanolysis, saponification occurs faster and soap concentration in biodiesel phase is higher than methanolysis [93]. Saponification if occurred would result in a reduction in ester yield as well as consumption of the catalyst. It was found that during ethanolysis of sunflower oil, 95% of sodium hydroxide initially loaded in the reactor was converted into sodium soap within 5 min. The soap formation not only lowers the ester yield but also complicates the glycerol separation step in the biodiesel purification process. In order for phase separation to occur, an additional step such as ethanol evaporation [94] or glycerol addition [95] is necessary. An alternative solution is to use mixtures of methanol and ethanol [66,96,97].

3.3. Effects of catalyst type

Type of catalysis is one of the most important parameters in transesterification reaction. Selection of catalyst is a crucial step

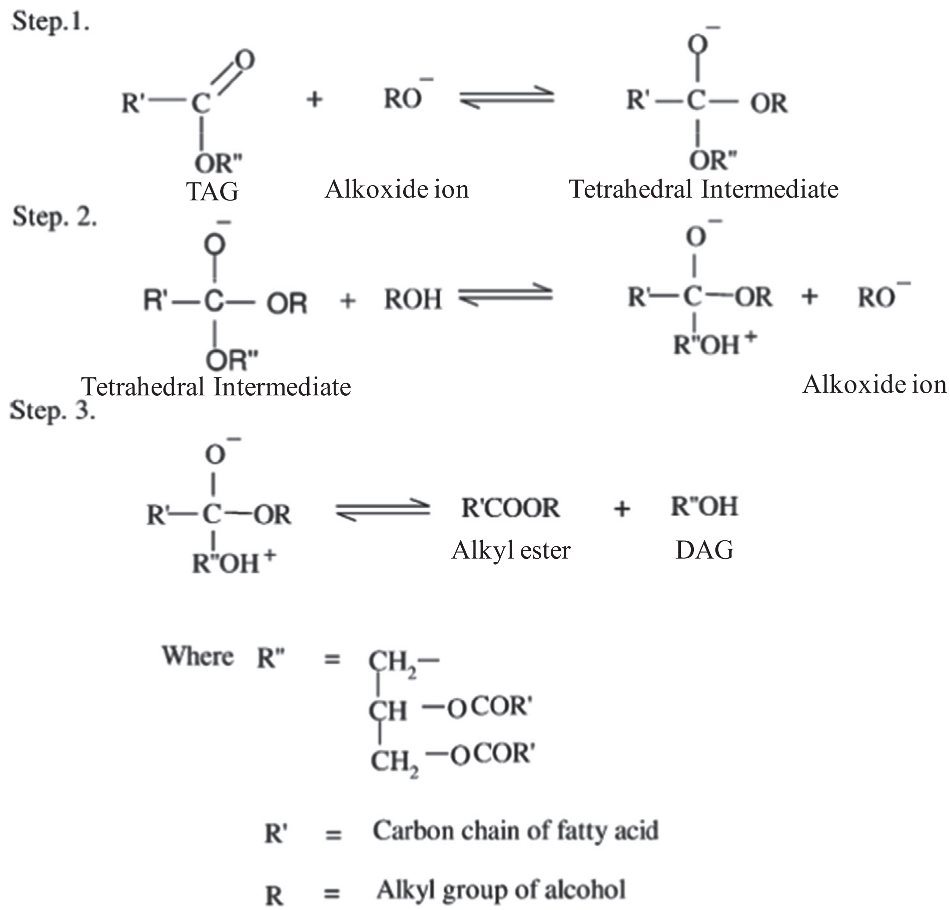


Fig. 5. Mechanism for homogeneous base catalysis in transesterification.

determining the outcome of the biodiesel production process and is greatly dependent on the type and quality of feedstock. Most commercial processes employ homogeneous base catalysts due to high reaction yield, short reaction time, low reaction temperature requirement, and beneficial economic of the catalysts [7]. Feedstock containing higher amounts of FFA and water such as used cooking oil, however, require incorporation of acid catalysis in the production process [66]. More recently solid catalysts are subjected to investigation because the use of these catalysts simplifies the biodiesel purification step, eliminates waste water generation, and renders continuous biodiesel production process possible [66,98,99]. However, further research and development is needed due to their lower catalyst activity as compared to that of homogeneous base catalysts which leads to a requirement of longer reaction time and usually higher reaction temperature. Enzymatic catalysis is another alternative as it neither produces soap nor waste water but has expensive operating cost and strict reaction conditions [100]. On the other hand, attempts have been made to carry out non-catalytic transesterification reaction under supercritical conditions [82–84]. The process does not require catalysts and has a short reaction time. However it requires extreme reaction temperatures and pressures, therefore the process is susceptible to polymerization [101]. Consequently, purification step becomes difficult due to the increase in viscosity. Each type of catalysis is discussed in the following sections.

3.3.1. Homogeneous base catalysis

Homogeneous base catalysis is most commonly used in commercial biodiesel production process. This is because the process offers high reaction yield (97% or more) in a short time (10 min to 2 h) with mild reaction temperatures (25–70 °C). The reaction mechanism involves 3 steps as shown in Fig. 5. The first step is the attack of alkoxide ion (methoxide ion in the case of methanol as reacting alcohol) to carbonyl carbon of the TAG molecule to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with alcohol to regenerate alkoxide ion. The last step involves rearrangement of the tetrahedral intermediate to form alkyl ester and DAG. This mechanism can be extended to the reaction of DAG and MAG in the same manner.

Examples of homogeneous base catalysis for transesterification are presented in Table 6. It is reported that homogeneous base catalysis in transesterification is much faster than homogeneous acid catalysis [73]. However, homogeneous base catalysis is limited to quality of the feedstock used in transesterification, i.e. acid value of lipid must be lower than 1 and all starting materials must be substantially anhydrous. Acid catalysts are more suitable if the feedstock contains higher amounts of free fatty acid and water such as used cooking oil. The most common homogeneous catalysts are hydroxides and alkoxides of alkali metals such as NaOH, KOH, $NaOCH_3$, $KOCH_3$. Ma et al. [63] found that hydroxide of alkali metal is more effective than alkoxide as NaOH and $NaOCH_3$ reached their maximum activities at 0.3 and 0.5 wt% with respect to beef tallow. Controversial results were reported by other researchers as $NaOCH_3$ was reported to be more effective than NaOH [68]. In the presence of acid, water is formed from free OH group in NaOH or KOH while methanol is formed instead of water if $NaOCH_3$ or $KOCH_3$ is used. When water is generated, it has several adverse impacts on the transesterification reaction as discussed in Section 3.1. In addition Mahajan et al. [116] showed that when $NaOCH_3$ was used, the acid value of the reaction product was significantly lower than that when NaOH was used. However, alkali metal alkoxides are less popular

Table 6
Examples of homogeneous catalysis on esterification and transesterification.

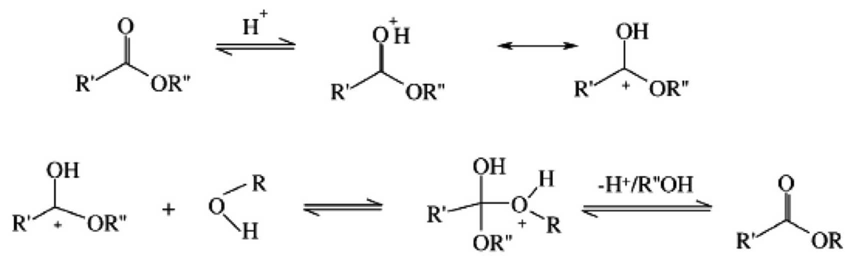
Feedstock	Catalyst	Alcohol	Alcohol to oil ratio	Temperature (°C)	Duration	Conversion/yield	Year	Reference
Base catalysis								
Vegetable oils	NaOH 1 wt% CH_3ONa 0.5 wt%	Methanol	6:1	60	1 h	93–99% Conversion	1984	[67]
Beef tallow	NaOH 0.3 wt% CH_3ONa 0.5 wt%	Methanol	6:1	65	15 min	60% Yield	1998	[62]
Vegetable oils	KOH 0.5 wt% CH_3ONa 0.25 wt%	C1–C4 Alcohol	6:1	25	40 min	87–96% Yield	2001	[88]
Waste vegetable oils	KOH	Methanol	–	60	1 h	95% Conversion	2002	[101]
Vegetable oils	KOH 1 wt%	Methanol	6:1	25	40 min	51–87% Yield	2004	[102]
Pongamia pinata	KOH 1 wt%	Methanol	10:1	105	1.5 h	92% Conversion	2005	[68]
Canola oil	NaOH 1 wt%	Methanol	6:1	45	15 min	98% Ester content	2006	[69]
Used fryling oil	NaOH 1.1 wt%	Methanol	7:1	60	20 min	94.6% Ester content	2006	[69]
Pongamia pinata	KOH 1 wt%	Methanol	6:1	65	2 h	97–98% Yield	2006	[103]
Canola oil	KOH 1 wt%	Methanol Ethanol	6:1	25–70	2 h	$>90\%$ Yield	2007	[95]
Waste fryer grease	H_2SO_4 2 wt% KOH 1 wt%	Methanol Ethanol	6:1	50–60	5–6 h	97% Ester content	2007	[65]
Jatropha	NaOH/KOH 1 wt%	Methanol	3:1	–	2–4 h	–	2007	[104]
Mixed canola and used cooking oil	KOH 1 wt%	Methanol Ethanol	6:1	50	2 h	98% Ester content	2008	[94]
Rapeseed	KOH 1 wt%	Methanol	6:1	65	2 h	95–96% Yield	2008	[71]
Sunflower	NaOH 1 wt%	Methanol	6:1	60	2 h	97.1% Yield	2008	[105]
Karanja	H_2SO_4/NaOH/KOH	Methanol	8–9:1	45	1 h	89% Yield	2008	[106]
Greenseed Canola oil	KOH 1 wt%	Methanol Ethanol	6:1	60	90 min	97% Ester content	2010	[96]
Coriander seed oil	Ch_3ONa 0.5 wt%	Methanol	6:1	60	90 min	94% Yield	2010	[107]
Acid catalysis								
Soybean	H_2SO_4 1 wt%	Butanol	30:1	117	3 h	–	1986	[72]
Soybean	H_2SO_4 3 wt%	Methanol	30:1	60	48 h	98% Conversion	1999	[73]
Madhuca indica	H_2SO_4 1% v/v	Methanol	0.3–0.35 v/v	60	1 h	98% Yield	2005	[108]
Rubber seed oil	H_2SO_4 0.5% by volume	Methanol	6:1	45	20–30 min	–	2005	[109]
Tobacco seed oil	H_2SO_4 1–2%	Methanol	18:1	60	25 min	91% Yield	2006	[110]
Waste frying oil	H_2SO_4 3.8:1 mole ratio	Methanol	24.5:1	70	4 h	99% yield	2006	[75]
Calophyllum inophyllum	H_2SO_4 0.65% by volume	Methanol	6:1	65	90 min	85% Yield	2007	[111]
Zanthoxylum bungeanum	H_2SO_4 2%	Methanol	24:1	60	80 min	98% Yield	2008	[112]
Tallow	H_2SO_4 2.5 wt%	Methanol	30:1	60	24 h	98.28% Yield	2008	[74]
Canola	$AlCl_3$	Methanol	24:1	110	18 h	98% Conversion	2009	[113]
Soybean	CF_3CO_2H 2.0 M Concentration	Methanol	20:1	120	5 h	98.4% Ester content	2009	[114]
High AV oil	H_2SO_4 4 wt%	Methanol	20:1	120	5 min residence time	99.5% Yield	2010	[115]

than hydroxides in large scale production due to their toxicity, higher price and disposal problems. When alkaline metal alkoxides and hydroxides are used as catalysts in methanolysis, the active catalytic species are the same, i.e. methoxide ion (CH_3O^-), therefore it is concluded that these catalysts are equally effective [89]. It was also reported that at 6:1 alcohol to oil molar ratio, the use of 0.5% $NaOCH_3$ is as effective as 1% NaOH [68]. The reaction yield can also be increased by using a two-step process, by separating and removing glycerol at the end of the first step [117]. An increase in reaction yield compared to the one step process stems from a shift in reaction equilibrium to the product side due to the removal of glycerol during the production process.

3.3.2. Homogeneous acid catalysis

In biodiesel production from feedstock containing high FFA and water content, acid catalysis is more suitable. This approach can be used to avoid saponification and FFA is directly converted to ester through esterification while glycerides are converted to ester through transesterification. Therefore, acid catalysts can be used to catalyze both esterification and transesterification while base catalysts only catalyze transesterification but not esterification [118]. The disadvantages of homogeneous acid catalysis are that it requires a high reaction temperature, an acid-tolerable reactor, and a longer reaction time due to slower rate of the reaction. The reaction mechanism is shown in Fig. 6. The first step is protonation of carbonyl group in the glyceride molecule which leads to carbocation. Then the attack of alcohol produces a tetrahedral intermediate. The elimination of glycerol backbone from this intermediate leads to the formation of ester. Although saponification can be avoided, water is still being generated during esterification of FFA (see Fig. 6). Water can then undergo hydrolysis which is reverse of esterification, however, unlike esterification, hydrolysis can occur in presence of either base or acid. The resulting carboxylate anion from hydrolysis shows little tendency to reaction with alcohol to form ester but reacts readily with K^+ or Na^+ in presence of a base to form a stable salt. Therefore it is essential to perform acid-catalyzed esterification and base-catalyzed transesterification separately.

Examples of homogeneous acid catalysts are H_2SO_4, H_3PO_4, HCl, BF_3, and CF_3CO_2H. Among these catalysts, H_2SO_4 is the most common catalyst as shown in Table 6 due to its good catalytic activity and simplicity in H_2SO_4/MeOH preparation as concentrated liquid H_2SO_4 can be added directly to methanol. The most common H_2SO_4 concentration used in esterification is 1–2%. HCl/MeOH which was introduced for esterification about half century ago but it is not a very popular choice due to its complexity in preparation of the solution, involving bubbling hydrogen chloride gas into methanol or adding acetyl chloride slowly to methanol



$R'' = hydrogen$ for esterification and R'' = OR' (or OH), OR' (or OH) for transesterification

$R' = carbon\ chain\ of\ fatty\ acid$

$R = alkyl\ group\ of\ alcohol$

Fig. 6. Mechanism for homogeneous acid catalysis in esterification and transesterification.

[118] so the common concentration is 5%. BF_3/methanol prepared by bubbling BF_3 gas into cooled methanol. BF_3 has an empty orbital that can accept a pair of electrons making it a Lewis acid. This catalyst can catalyze esterification much faster than transesterification and it is reported that FAME can be prepared from fatty acids using this catalyst within a very short time (10 min) using 6–14% catalyst loading. Due to its superior activity and short reaction time, the American Oil Chemists' Society (AOCS) has adopted BF_3 in the official method for preparing methyl ester from fatty acids (AOCS Ce 2–66). However, BF_3 is not used as widely in literature as H_2SO_4 because it is expensive, toxic, and has a limited shelf life [118]. Diazomethane (CH_2N_2) is not classified as an acid catalyst but rather as a strong methylation reagent. Despite its inability to catalyze transesterification, diazomethane in ether esterifies free fatty acid at a much faster rate when compared to acid catalysts. However, its shortcomings such as highly toxic, short shelf life and potential explosivity have prevented it from being used spreadingly like other catalysts.

3.3.3. Heterogeneous base catalysis

Homogeneous base catalysts have gained significant attention from numerous biodiesel researchers. This is because the catalyst removal process is simple and does not create waste water that is generated during the catalyst removal step when homogeneous catalysts are used. In addition, heterogeneous catalyst can be regenerated and reused, rendering biodiesel production in a continuous processes possible. However, the use of such catalyst is limited by free fatty acid usually contained in low quality feedstock such as used cooking oil. Nevertheless, this catalyst can be used when a good quality feedstock is used and several advantages such as catalyst reusability, simplicity in catalyst removal, low reaction temperature requirement, and short reaction time still entice several researchers to investigate this area. The mechanism scheme of heterogeneous base catalysis using CaO as an example catalyst is shown in Fig. 7. The first step involves the extraction of H^+ from H_2O to form surface OH^- on the basic site of CaO (Eq. (1)). Then H^+ is extracted from methanol to form methoxide ion and water (Eq. (2)). Also, methanol can adsorb dissociatively on CaO (Eq. (3)). The next step is an attack of the adsorbed methoxide ion to acylglycerol molecule to form tetrahedral intermediate (Eq. (4)) which is protonated afterward (Eq. (5)). The tetrahedral intermediate can also react with methanol to generate methoxide anion (Eq. (6)). In the last step, the rearrangement of the tetrahedral intermediate leads to the formation of methyl ester and glycerol or acylglycerol.

Examples of heterogeneous base catalysis are illustrated in Table 7. Common heterogeneous base catalysts are those of alkaline earth metal oxides such as MgO, CaO, SrO, and BaO. BaO is not suitable in methanolysis because it dissolves in methanol and creates leaching problems while SrO reacts strongly with CO_2 and water in the air to form $SrCO_3$ and $Sr(OH)_2$. The catalytic activity of MgO is not very high due to the low basic strength of MgO leaving CaO to be the most attractive alkaline earth metal oxides catalyst. Alkali metals such as Li, Na, K can be used to promote these catalysts. It is shown that pure $LiNO_3$ is inactive and CaO alone has low activity towards transesterification of tributyrate [120]. Proper impregnation of $LiNO_3$ on CaO results in highly dispersed monolayer Li^+ on CaO that exhibits high catalytic activity on transesterification. However, if too much $LiNO_3$ is added, the resulting catalyst is associated with the non-dissociative NO_3^- ions over CaO surface and the formation of $LiNO_3$ multilayers. These inactive species have proven detrimental to the catalytic activity of Li/CaO catalyst. In addition Li/CaO has higher basic strength and activity as compared to Na/CaO and K/CaO [140]. This is because the small size of Li^+ ion makes it easier to be inserted more properly in the CaO framework creating oxygen gaps that contribute to the basic strength of the catalyst.

Alternatively, K_2CO_3 supported on Al_2O_3 can be used in transesterification. It is one of the most common catalysts in many organic chemical reactions such as isomerization, alkylation, and transesterification. This is because K_2CO_3/Al_2O_3 has strong basic strength and the catalytic activity of solid base catalysts depend greatly on basicity of the catalyst rather than the surface area [121]. The catalytic activity of K_2CO_3/Al_2O_3 is superior to metal promoted CaO and SrO and only second to alkali metal promoted BaO. Unlike alkali metal promoted BaO, leaching of K_2CO_3/Al_2O_3 is negligible.

3.3.4. Heterogeneous acid catalysis

Heterogeneous acid catalysts are the most promising catalysts for biodiesel production and are expected to dominate commercial biodiesel industries in the coming years. This is due to the simplicity in biodiesel purification step that eliminates waste water, reuseability that make continuous process possible, and their ability to handle low quality feedstock with high FFA content via simultaneous esterification and transesterification. The disadvantage of heterogeneous acid catalysts is the lower catalytic activity leading to requirements of higher reaction temperature (~200 °C) and reaction time (8–20 h). Catalyst leaching is another main issue for this type of catalyst. If the catalyst leaches into biodiesel, purification will be required to remove the contaminated catalyst and thereby generating waste solvent and increasing the biodiesel production cost. In addition, catalyst reusability or catalyst deactivation is usually studied for this type of catalyst. The simultaneous esterification–transesterification reaction mechanism is shown in Fig. 8. In the esterification reaction, FFA reacts with methanol to form methyl ester. The first step involves

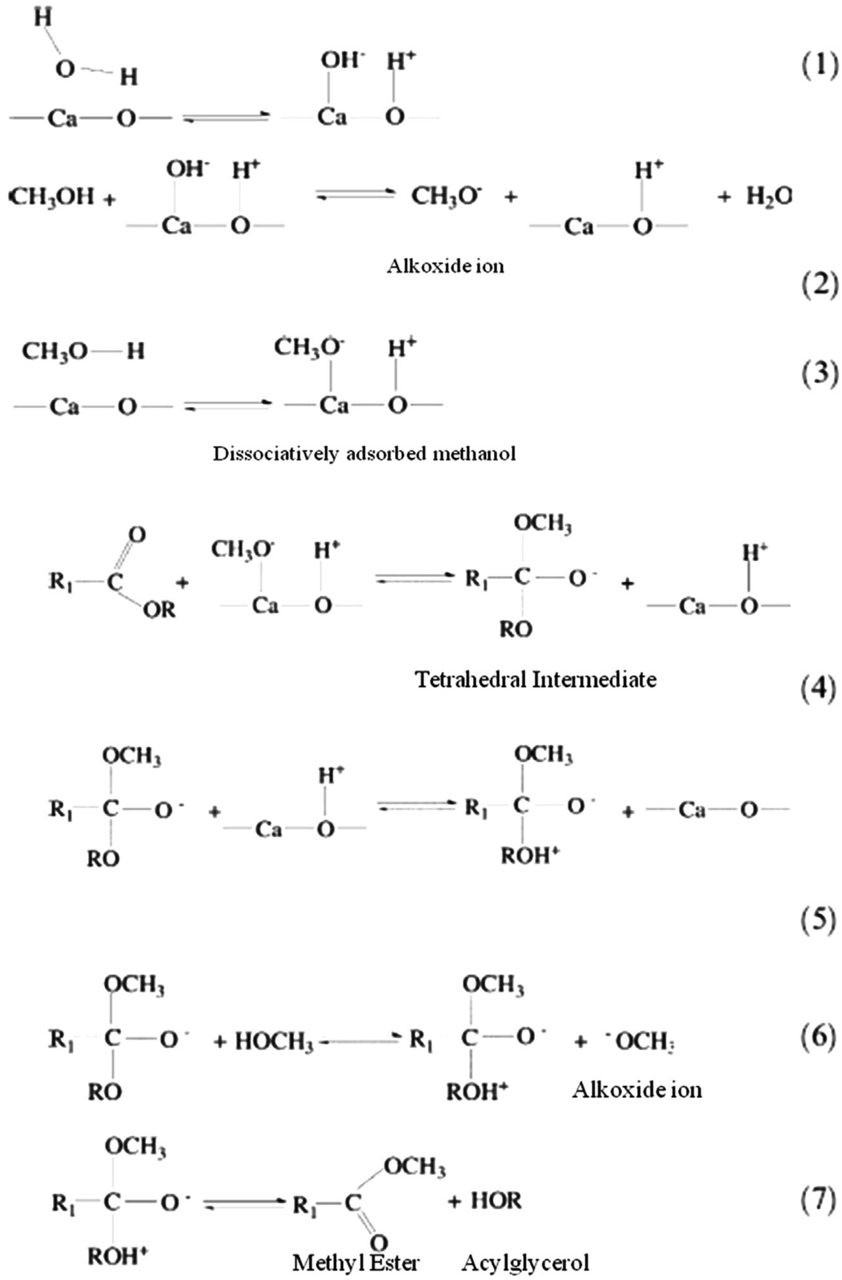


Fig. 7. Mechanism for heterogeneous base catalysis in transesterification.

an adsorption of FFA on the acidic site on the catalyst surface. The interaction between FFA and the acidic site leads to carbocation. Then an attack of methanol produces a tetrahedral intermediate. Finally, methyl ester is formed as a result of elimination of a water molecule from the tetrahedral intermediate. In transesterification, acylglycerol including tri-, di-, and monoglyceride reacts with methanol to form methyl ester. The reaction mechanism occurs in a similar manner as that described in the esterification reaction. The formation of methyl ester stems from an elimination of diglyceride, monoglyceride, and glycerol from the tetrahedral intermediate when triglyceride, diglyceride, and monoglycerideare adsorbed in the acidic site, respectively. Various types of heterogeneous acid catalysts are available for esterification and transesterification as shown in Table 7 and these catalysts are discussed as follows.

Ion-exchange resins such as Amberlyst series and Nafion silica composite solid acid catalysts are one of the first solid acid catalysts introduced for biodiesel production application [127,141]. These resins have low catalytic activity and therefore extreme reaction temperature is required. Unfortunately, resins usually have low thermal stability (< 140 °C) and therefore the reaction was conducted at a mild temperature of 60 °C, which is resulted in a low reaction conversion (74%). Alternatively, silica matrix of mesoporous solids can be used, but the catalytic activity is low. Metals such as aluminum, zirconium, titanium, or tin ions can be added to improve catalytic activity on esterification and transesterification. However, metal-doped materials tend to behave like weak acids of which high catalytic activity is not exhibited. To improve catalytic activity of the catalyst, high dispersion of a strong acid species on interior surfaces of mesoporous supports is required.

Tungsten loaded catalyst is an interesting catalyst. WO_3/ZrO_2 is used as a catalyst in esterification of palm oil and a conversion of 98% is obtained [142]. Upon its formation, hydrous zirconia contains very small regions of tetragonal structure exhibiting the (101) phase

Table 7
Examples of heterogeneous catalysis on esterification and transesterification.

Feedstock	Catalyst	Alcohol to oil ratio	Temperature (°C)	Duration (h)	Yield (%)	Leaching	Year	Reference
Base catalysis								
Rapeseed	MgO	22:1	Reflux	22	94	n/a	2001	[118]
Rapeseed	BaO	6:1	Reflux	1	96	n/a	2001	[118]
Gylceryl tributyrate	Li/CaO	n/a	60	0.5	~100	No	2004	[119]
Karanja	Li/CaO	12:1	65	8	95	n/a	2006	[103]
Canola	K_2CO_3/Al_2O_3	11.48:1	60	2	94	Yes	2007	[120]
Rapeseed	$K/KOH/Al_2O_3$	9:1	60	1	85	Yes	2008	[121]
Soybean	Fe3+/Mg–Al HTC[a]	6:1	80	1	38	Yes	2008	[122]
Jatropha	$X/Y/MgO/Al_2O_3$	10:1	reflux	3	97	n/a	2008	[123]
Rapeseed	K_2CO_3/Al_2O_3	15:1	50	3	99	n/a	2010	[124]
Sunflower	La_2O_3/ZrO_2	30:1	200	5	85	n/a	2010	[125]
Acid catalysis								
Babassu	Amberlyst 15	300:1	60	8	74	n/a	2005	[126]
Soybean	$WO_3/ZrO_2/Al_2O_3$	40:1	250	20	90	n/a	2006	[127]
Canola (20% FFA)	TPA/HZ[b]	9:1	200	10	90	no	2006	[66]
Palm kernel	SO_4^{2-}/ZrO_2	6:1	200	1	95	n/a	2006	[128]
Cottonseed	SO_4^{2-}/TiO_2	12:1	230	8	96	n/a	2007	[129]
Palmitic acid	$SO_4^{2-}/ZrO_2/SiO_2$	10:1	68	6	89	n/a	2007	[130]
WCO[c]	ZS[d]/Si	18:1	200	10	98	no	2008	[97]
WCO[c] (28% FFA)	SO_3H/starch	30:1	80	8	92	n/a	2008	[131]
Cottonseed	SO_4^{2-}/TiO_2-SiO_2	9:1	200	6	92	n/a	2008	[132]
WCO[c] (15% FFA)	WO_x/Al_2O_3	n/a	110	2	97	n/a	2009	[133]
Palm (5% FFA)	Arene-SO_3H/SBA15	20:1	140	4	95	n/a	2010	[134]
WCO[c]	TPA/Nb_2O_5	18:1	200	20	92	no	2010	[98]
Rapeseed	Fe–Zn DMC[e]	16:1	160	8	98	n/a	2010	[135]
Vegetable oil	Fe–Zn DMC[e]	15:1	170	8	84–99	n/a	2010	[136]
Cottonseed	SO_3H/starch	20:1	80	12	97	Yes	2011	[137]
Vegetable oil	Fe–Zn DMC[e]	16:1	170	8	98	n/a	2011	[138]

[a] HTC=Hydrotalcite.
[b] TPA=tungstophosphoric acid, HZ=hudrous zirconia.
[c] WCO=waste cooking oil.
[d] ZS=zinc stearate.
[e] DMC=double metal cyanide.

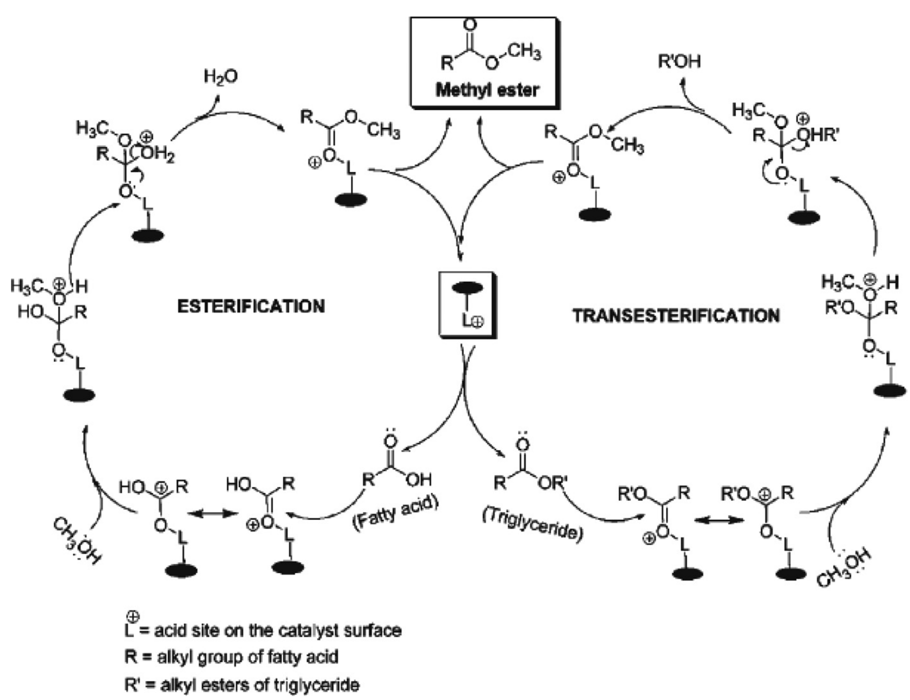


Fig. 8. Mechanism for heterogeneous acid catalysis in esterification and transesterification.

that can be observed in the XRD patterns. These tetragonal crystallites grow as hydrous zirconia is thermally treated and are transformed into the thermodynamically stable monoclinic phase during cooling. When an interacting species such as WO_3 is presented, the phase transition is somewhat hindered and the tetragonal phase is maintained. However, if too much WO_3 is added, the catalyst becomes amorphous due to excess coverage of WO_3 species on ZrO_2. The presence of monoclinic phase of zirconia has adverse effects on catalytic activity and the tetragonal phase is therefore preferred. However, the presence of tetragonal zirconia is not the

only criterion for good catalytic activity of the catalyst as the co-existence of amorphous WO_3 is also required. It was found that the catalytic activity of WO_3/ZrO_2 catalyst is provided by the interaction between amorphous WO_3 and crystalline ZrO_2. In addition to zirconia, Al_2O_3 has been used as support due to its high surface and large pore size that can accommodate TAG molecules with long fatty acid chains. A 98% ester yield was observed from transesterification of waste cooking oil using WO_x/Al_2O_3, however, the acid value was observed to be 4.7 higher than that specified in biodiesel standards [134].

Sulfated catalyst is another choice of interested catalysts. By using a conventional homogeneous acid H_2SO_4 as a precursor, SO_4^{2-} on ZrO_2 and TiO_2 can be obtained and the reaction yields 95–96% conversion [129,130]. The catalytic activity of sulfated zirconia (SZ) can be further increased by dispersing it onto mesoporous silica materials such as MCM-41 or SBA-15, thus increasing dispersion and acid sites. SBA-15 is a preferred choice in esterification and transesterification due to its larger pore size to facilitate the long chain fatty acids. The doped zirconia on SBA-15 (unsulfated ZrO_2/SiO_2) shows low acidity and its acidity can be enhanced by addition of sulfur. It is believed that addition of sulfur results in formation of tetragonal ZrO_2 and enhances the phase segregation by extracting zirconia to the surface of the mixed oxides and stabilizes the tetragonal phase [131]. However, if too much sulfur is added ($>5\%$), a monoclinic phase of zirconia is formed in addition to the tetragonal phase and this should be avoided [143]. Also, the hydrophilicity of SBA-15 surface is partially responsible to catalyst stability. In general, water formed during esterification is adsorbed on acid sites resulting in a lower concentration of acidic sites available for the reaction. However, this water can be readily adsorbed on the neighboring silica surface of SBA-15 and some acidic sites can thus be recovered. Despite its high activity, SZ-type catalyst shows sulfate leaching problem, which is enhanced by hydrolysis. To counter this problem, chlorosulfonic acid is used as an alternate acid to sulfuric acid for SZ catalyst preparation. The catalyst was tested in esterification of acetic acid with *p-tert*-butylcyclohexanol and no leaching was observed [144]. More recently, high reaction conversion (92–97%) was obtained using sulphated starch catalyst [132,138]. An interesting point about starch derived catalyst is that the reaction requires a relatively low temperature (80 °C); however, sulfate leaching has been observed.

Heteropolyacids (HPAs) is later on introduced as a potential solid acid catalyst for biodiesel production. These acids are comprised of hydrogen, oxygen, metal such as tungsten, molybdenum, vanadium, and a *p*-block element such as silica, phosphorous, or arsenic. The two main HPA structures are the Keggin structure ($H_nXM_{12}O_{40}$) and Dawson structure ($H_nX_2M_{18}O_{62}$) where X and M represent *p*-block element and metal, respectively. The Keggin structure is self-assembled in acidic aqueous solution and is a preferred structure as it is thermally stable and has high acidity. In the Keggin structure, the heteroatom (X) is located at the center of the molecule, linked with 4 oxygen atoms to form a tetrahedral, and is surrounded by 12 octahedral MO_6 units that are linked to one another by neighboring oxygen bridge. This structure allows hydration and dehydration to occur without significant changes in structure and therefore it is thermally stable and can be used in a reaction under extreme temperatures (up to 400–500 °C). The disadvantages of the Keggin-type HPA are low specific surface area and solubility in polar media but these can be overcome by dispersing it on a high surface area support. Both unsupported and MCM-41 supported HPA have been used as an acid catalyst in esterification of acetic acid at 110 °C giving 95% conversion [145]. It was found that the supported HPA is more active than the unsupported HPA since the high dispersion of HPA on MCM-41 internal surface leads to high population of available acid sites. However, MCM-41 supported HPA is more vulnerable to water than unsupported HPA because water formed during esterification leads to HPA migration to outer surface, pore blocking and catalyst sintering. Hydrous zirconia (HZ, $ZrO_2\cdot nH2O$) has been used as a support for 12-tungstophosphoric acid (TPA, one of the Keggin-type HPAs). TPA/HZ was tested for its catalytic activity in esterification and transesterification of canola oil containing FFA up to 20% at 200 °C for 10 h duration and it gave a 90% ester yield [66]. It was found that esterification was catalyzed at a faster rate than that of transesterification. This is because esterification route involves a simple reaction step while transesterification route is composed of a series of reversible reaction steps. More recently, Nb_2O_5 was reported as an effective support for TPA [99]. Under the optimized conditions of 18:1 alcohol to oil ratio, reaction temperature of 200 °C and 20 h reaction duration, 92% ester yield can be obtained from transesterification of waste cooking oil without catalyst leaching.

More recently, Fe-Zn double metal cyanide catalysts (DMC) have been investigated for transesterification of vegetable oil [136,137,139]. Cyanide is a highly toxic chemical compound containing cyano group ($-C\equiv N$). They have general formula: $K_4Zn_4[Fe(CN)_6]_3\cdot xH_2O$ where $x=6$–12 and the catalyst exhibits highest activity when $x=6$. The Fe and Zn ions are linked through cyano groups. The most interesting feature of this catalyst is its hydrophobicity as it can tolerate water content in the feedstock oil up to 20% without significant loss in catalytic activity [137]. It is found that the rate of esterification is faster than that of transesterification, in line with other heterogeneous acid catalysts such as TPA/HZ. The catalyst is tested with various vegetable oils and shows promising catalytic activity (84–99% conversion) and can be reused without loss in catalytic activity and no purification is required for catalyst regeneration. However, when non-edible oil such as jatropha, rubber seed, and pinnai oil is used as feedstock, the acid value of the resulting biodiesel is higher than that specified in biodiesel standards and further catalyst leaching investigation is required. Another catalyst such as zinc stearate (ZS) on silica (Si) was investigated. ZS ($Zn(C_{18}H_{35}O_2)_2$) is a zinc soap that is not soluble in polar solvents but soluble in aromatic hydrocarbons when heated. When ZS/Si is tested on transesterification of waste cooking oil, a 98% ester yield can be obtained [98]. In addition, catalyst leaching is not detected and the catalyst can be reused without significant loss in its activity. However, the resulting biodiesel shows acid value of 3.3, higher than those specified in biodiesel standards. In summary, further development in heterogeneous acid catalysis is required especially in terms of ester yield, acid value of the product, and catalyst leaching.

3.4. Effects of reaction time, temperature, and the reaction kinetics

In general, conversion and yield increase as reaction time increases. The reaction starts with two phases: alcohol and oil. Once the reaction is initiated, DAG and MAG are formed as the reaction intermediates and act as surfactants to enhance the mass transfer of TAG into methanol. At this point, the reaction mixture can occur either in one or two phase depending on the amount and type of alcohol used in the reaction as well as the reaction conditions. Then glycerol is formed as the reaction by-product and separates out as an additional phase. If the reaction is catalyzed homogeneously, the separation of glycerol often leads to catalyst dissolving in glycerol phase, which lowers catalyst concentration in the reaction mixture and therefore slows the reaction rate.

The rates of the reaction and rate constants are often used in kinetic studies in order to examine how fast the reaction proceeds. These kinetic parameters are sometime evaluated based on shunt (overall) reaction mechanisms in which 3 mol of TAG react with 3 mol of alcohol to yield 3 mol of ester and 1 mol of glycerol [146]. Although, the kinetic models can be simplified using the shunt reaction mechanism, it is highly unlikely that three molecules of

methanol would simultaneously attack the TAG molecule to form three molecules of methyl ester. The shunt mechanism is easily disproved by the formation of DAG and MAG which is widely reported in the literature. Therefore, the kinetic models should be derived based on three consecutive reversible reaction steps and the rate constants of each reaction step are usually different. The values of the rate constants indicate the rates of the corresponding reaction step as well as reversibility of each step. Moreover, they can be used to determine the rate determining step (RDS) that controls the kinetics of the overall transesterification. The proposed reaction mechanism consists of an initial mass transfer-controlled region followed by a kinetically controlled region [79,146]. The mass transfer effect is referred to the period where there is no reaction going on and yet is recorded as "reaction time" during an experiment. This period is associated with the time that triglyceride molecule spends in order to move into methanol phase and collides with the methanol molecule. This period occurs at the initial part of the reaction and is often referred to as "mass transfer-controlled region". The initial mass transfer region alters the observed kinetic data and therefore needs to be minimized by means of rigorous mechanical agitation [80], co-solvent aid [148], or supercritical conditions [149]. Results from literature suggest that transesterification of vegetable oils with low alcohol to oil ratio (6:1) using homogeneous base catalysts follows second order kinetics [73,78,80,147]. The reaction step TAG to DAG is often found to be the rate limiting step that controls the kinetics of the overall reaction. In addition, the rate constant of the reverse reaction MAG to GL is usually lowest due to the phase separation of glycerol. However this reaction can still take place at the glycerol-methyl ester interface rendering a small positive value to the rate constant.

Transesterification is strongly dependent on reaction temperature and is favored at high temperatures. In mass transfer controlled region, higher temperature leads to higher energy state of the reacting molecules that can be translated into faster molecular vibration and movement, thus the reacting molecules have more chance to collide with one another. In a kinetically controlled region, temperature dependency of the reaction rate is often used to calculate the activation energy of the reaction by plotting logarithm of the rate constant versus the reciprocal of the reaction temperature [150]. The equation is known as the Arrhenius equation (see Eq. (1)).

$$k = Ae^{(-E_a/RT)} \quad (1)$$

where k is the rate constant; A is pre-exponential factor; E_a is the activation energy; R is the gas constant; and T is reaction temperature. The activation energy is referred to the minimum energy that is required for a reaction to take place. From Eq. (1), if the reaction temperature is increased, the rate constant will also increase and therefore the reaction will proceed at a faster rate.

A homogeneous alkali-catalyzed transesterification can be performed at a temperature as low as room temperature. However, higher temperatures are usually employed especially when an acid catalyst is used. Nevertheless, the reaction temperature should be kept below boiling point of the corresponding reacting alcohol that is 65 °C for methanol and 78 °C for ethanol. Heterogeneous acid catalysis, however, usually requires extreme reaction temperature (up to 220 °C). If the reaction is operated at temperatures higher than the boiling point of the corresponding reacting alcohol, pressure is needed to be applied to the reaction mixture in order to maintain the reacting alcohol in liquid state.

3.5. Techniques for monitoring transesterification

In transesterification, TAG is converted to ester step-wise through the formation of intermediates DAG and MAG. The

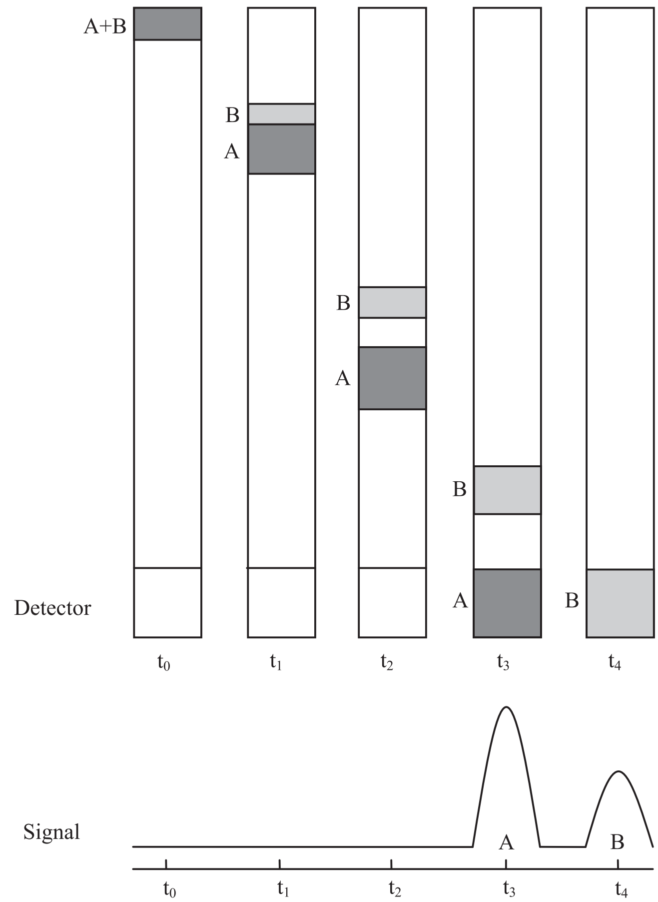


Fig. 9. Chromatographic separation of component A and B and their corresponding output signals.

formation of each individual compound should be monitored closely. Various techniques have been developed in order to monitor the reaction and an acquisition of more detailed information requires more sophisticated, expensive, and time consuming techniques and vice versa. Chromatography techniques are most commonly used because they offer comprehensive perception during transesterification progress and detailed information required for quality control of the product (Fig. 9). More recently, nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectrometry have been employed for monitoring transesterification. Cheaper methods such as thin layer chromatography (TLC) without detector, viscometer, titration, and the 3/27 conversion test have also been used, however shortcomings of these methods involve the lack of quantitative analysis.

3.5.1. Gas chromatography

Gas chromatography technique has been developed to simultaneously determine glycerides and ester in a single run using a 10–15 m of capillary DB-5 column coated with 0.1 μm film equipped with FID [80]. TAG, DAG, MAG, and methyl ester concentrations were measured using a GC model agilent 7890A equipped with J&W 123-5711 DB-5HT column (15 m × 320 μm × 0.1 μm; 400 °C max temperature), cool on-column Inlet with track oven temperature mode, 7.6 psi, 1 μL injection volume, and FID Detector, at 380 °C, 40 mL/min H_2 flow rate, and 400 mL/min air flow rate. The program was set to start at 50 °C, ramp from 50 to 230 °C at 5 °C/min, and ramp from 230 to 380 °C at 30 °C/min and hold for 18 min with a total run time of 1 h. Calibration curves showed sufficient linearity with the correlation coefficient of more than 0.99 [151]. In principle,

TAG, DAG, MAG, ester, and glycerol can be analyzed on a highly inert column coated with apolar stationary phase without derivatization [53]. However, in most cases, derivatization is required because diglyceride and monoglyceride contain free hydroxyl groups, which cause difficulty in quantifying these materials well in GC. Trimethylsilylation (derivatization) of DAG, MAG and glycerol causes changes in their structure and polarity by eliminating the free hydroxyl groups and therefore improving peak shape and peak separation. The dericatizing agent can be either N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) or N,O-bis(trimethysilyl) trifluoroacetamide (BSTFA) and the derivatizing procedure is given in the ASTM D6584 method. Internal standards such as 1,2,4-Butanetriol and 1,2,3-Tridecanolylglycerol (tricaprin) are usually used for 2 purposes: peak identification and quantification. In the identification step, retention time of analytes peaks are compared with those of internal standards and identified through relative retention time. This step may seem unnecessary if the corresponding standard sample is available. In quantification, an internal standard is usually used to correct the loss of standard mixture during sample preparation and injection.

3.5.2. Liquid Chromatography

The main advantage of liquid chromatography (LC) over GC is its simplicity in the sample preparation step as sample derivatization and internal standards are not required. Earlier LC was carried out with the gravity flow method using a glass column packed with solid particles (diameter more than 150–200 μm) coated with an adsorbed liquid as stationary phase. It is well known that the column efficacies can be improved greatly by reducing the size of the packed particles, which gives rise to the new sophisticated technology using column with packing particles having diameter as small as 3–10 μm and the instrument is operated at high pressure. High performance liquid chromatography (HPLC) was then named to distinguish this new technology from the original gravity flow method. Today, all liquid chromatography is operated at high pressure and HPLC and LC are used interchangeably [152]. HPLC can be used for a wide range of chemicals and the LC mode should be selected carefully based on solubility and molecular mass of the analytes. Ion exchange LC is used for water soluble ionic compounds while normal phase and reverse phase LC (bonded phase LC) can be used for soluble inorganic solvent such as hexane and methanol, respectively. In bonded phase LC, the stationary liquid is not soluble in the mobile phase liquid and is kept stationary by chemical bonding resulting in highly stable packings. In earlier times, LC technique was based on highly polar stationary phase and a relatively nonpolar solvent known as mobile phase and this LC mode is now known as normal phase chromatography. Later on, reverse phase chromatography was introduced in which the stationary phase was nonpolar and mobile phase was a polar solvent. Bonded phase packing is classified as normal phase when the coating is polar and as reverse phase when the coating is nonpolar. In oils and fats, they are relatively nonpolar and are more soluble in hexane than methanol, therefore normal phase LC finds its use more often than reverse phase. Size exclusive chromatography (SEC) is a separation technique based on molecular size rather than polarity of the analytes. It is particularly applicable to high molecular mass species that are soluble in organic solvents such as tetrahydrofuran (THF) therefore it is widely used for the analysis of biodiesel sample containing TAG, DAG, MAG, fatty acids and esters. The column can be coated with hydrophilic or hydrophobic gel and it is sometime called gel permeation chromatography (GPC). The packing gel may be silica or polymer particles containing a network of uniform pores through which the solute and solvent molecules can diffuse in and molecules of analytes are effectively trapped in these pores. Compounds with molecular size larger than the average pore size of packing are excluded and therefore are the first to be eluted. Smaller molecules permeate throughout the pore maze and are trapped for longer time and therefore are eluted at a later time. Various LC are available for use with LC. The UV detector is used for absorption measurements of eluents from chromatographic column at single or multiple wavelengths. The absorption intensity is measured and calculated for absorbance that is shown in a chromatogram as a function of time. Application of an UV detector is limited to compounds that can absorb UV at a specific wavelength, i.e., acylglycerols have weak absorbance at wavelengths higher than 220 nm [153]. Reflective index detector (RID) continuously measures reflective index of the effluent and is used in general as it is reliable. Since RID is relatively insensitive, it is not affected by flow rate but its application is limited to the measurement of analytes at higher concentration as compared to other detectors. In evaporative light scattering detector (ELSD), the column effluent is continuously evaporated and the light scattering of the resulting aerosol is measured. ELSD is significantly more sensitive than RID with detection limit of 0.2 ng/μL but the mobile phase is limited to volatile components.

SEC equipped with RID has been used to quantify acylglycerols and esters of alcohol ranging from C_1 to C_4 [24]. A Hewlett-Packard 1100 series (HPLC–SEC) was used with two Phenogel 5 μ 100 A 300 × 7.80 mm 5 μm columns in series. The guard column is used to protect analytical columns by removing particulate matters and sample components that bind irreversibly to the stationary phase. The packing components are identical or similar to those of the analytical column but the particle size is larger to minimize pressure drop. THF was used as a mobile phase at one ml/min for 25 min. The operating parameters used were as follows: injection volume five μl; column temperature 24 °C; and detector temperature 35 °C. Analysis of glycerides, fatty acids, and esters was compared with that using HPLC equipped with various detectors including UV detector, ELSD, and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) detector [153]. The solvent systems used in this work are rather complicated including: (1) mixtures of methanol (A) with 5:4 2-propanol/hexane (B) from 100% A to 50:50 A:B – a non-aqueous reversed phase (NARP) solvent system and (2) mixtures of water (A), acetonitrile (B), and 5:4 2-propanol/hexane (C) in two linear gradient steps (30:70 A:B at 0 min, 100% B in 10 min, 50:50 B:C in 20 min, and last isocratic 50:50 B:C for 5 min). In APCI-MS and ELSD, sensitivity of individual TAG decreased with increase in the number of double bond. Sensitivity of UV detection is also different for each individual TAG, and APCI-MS was concluded to be the most suitable detector because it gave additional structural information about acylglycerols. Komers et al. [154] employed HPLC for quantification of TAG, DAG, MAG, and esters using UV detection at a wavelength of 205 nm. The glass column 150 × 3 mm with pre-column 30 × 3 mm, both packed with C-18, particles with diameter 7 mm and the mobile phase A (acetonitrile: water 80:20), B (acetronitrile), C (hexane:2-propanol 40:50) with 0–2 min – 100% A, 2–12 min – change to 100% B, 12–22 min – change to 50% B and 50% C, 22–29 min – change to 100% B, 30–32 min – change to 100% of B, 32–33 min change to initial 100% A.

3.5.3. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) technique involves the measurement of absorption of electromagnetic radiation in the radio frequency (~4 to 900 MHz) in which nuclei of atoms rather than outer electrons are involved in the absorption process. It is necessary to place the analyte in an intense magnetic field in order to cause nuclei to develop an energy state strong enough for absorption to occur. The most commonly used NMR technique in biodiesel analysis is proton NMR or ^{1}H NMR in which the

adsorption on protons is measured. Equivalent nuclei of proton do not interact with one another to give multiple absorption peaks, i.e., three protons in methyl group give rise to one peak rather than splitting among themselves to give multiple peaks. Gelbard et al. [155] employed ^{1}H NMR to measure methyl ester yield from rapeseed oil transesterification. The yield was calculated based on the absorption area ratio of methoxy and methylene protons. ^{13}C NMR was used in comparison to ^{1}H NMR to determine unsaturated fatty acid composition via absorption of allyic and divinyl carbons [156]. In addition, ^{1}H NMR spectra were obtained at 400 MHz for monitoring two stage transesterification of canola oil where the replacement of glycerol with methanol was shown [3]. More recently, polyunsaturated fatty esters were identified and quantified based on ^{1}H NMR spectra obtained at 300 MHz [156]. It was reported that the signal due to protons of ester group OCH_3 and long alkyl chain ($–CH_2$)n are indicated at 3.65 and 1.27 ppm, respectively, while signals from methyl groups at 0.875, 0.90 and 0.97 ppm are due to saturated, mono- and di-unsaturated, and polyunsaturated fatty acids (3 double bonds), respectively. The polyunsaturated fatty ester percentage was calculated based on integral intensity of the PUFA region from 0.9 to 1.02 ppm and the average of percentage of methyl protons present in methyl esters of unsaturated fatty acids containing three or more double bonds such as linolenic (C18:3), EPA(C20:5), DHA (C22:6) etc.

3.5.4. Infrared spectrometry

Method for monitoring transesterification can be established by analyzing spectra corresponding to biodiesel, the feedstock oil, and intermediate samples at 25, 50, 75% conversion [157]. Near Infrared (NIR) has been used for monitoring transesterification of soybean oil, and absorbance at 6005 and 4428 cm^{-1} gave distinguishing results of TAG and methyl ester [158]. It is found that NIR results are in good agreement with those obtained from ^{1}H NMR [158]. More recently, FTIR (mid IR) has also been used to monitor transesterification of *Cyanara cardulus*, cotton, sunflower, and sesame oil [159]. The absorption peak at 1200 cm^{-1} is associated with $O–CH_3$ stretching which is only present in methyl ester and not in TAG, and used primarily for quantitative purpose.

3.5.5. Other methods

Since the above mentioned techniques are not always available, various cheaper methods have been used to monitor transesterification. Thin layer chromatography (TLC) has been used for separation and confirmation of various lipid classes such as glycerides, free fatty acids, and esters [160,161]. A droplet of the sample is used on the TLC plate with mobile phase consisting of a mixture of hexane, diethyl ether, and a small quantity of formic or acetic acid to ensure that fatty acid migrates successfully. Complex lipids such as phospholipids and glycolipids will remain at the origin point. TLC offers a simple, fast, and cheap method to confirm the formation of specific individual compound during the course of the reaction but these compounds are not determined quantifiably without detection systems such as the flame-ionized detector (FID). With FID, these compounds can be quantified properly but the method becomes more cost-intensive. A simpler method to estimate the progress of the reaction is a measurement of changes in viscosity of the reaction mixture [162]. The principle of this method is based on the differences in viscosity of the reactant (TAG) and the product (ester). While transesterification may be monitored using viscosity, acid value is commonly used as means to determine progress in esterification. The so-called “3/27 conversion test” is used widely in home-made biodiesel industry where cost-intensive techniques such as chromatography and spectroscopy are not available. This method employs the fact that methyl ester is more soluble in methanol than TAG. In the 3/27 conversion test, 3 ml of biodiesel is added to 27 ml of methanol at a temperature around 20 °C and the mixture is shaken [163]. If TAG is present in the biodiesel sample, it will settle out of methanol phase as it is not soluble in methanol. This method can be used to roughly determine TAG conversion during transesterification; however measurement of DAG and MAG conversion is not applicable using this method.

3.6. Post reaction treatment

Transesterification products consist of biodiesel and glycerol that are contaminated with alcohol and catalyst and post reaction purification of biodiesel is a crucial step to ensure product quality that meets standard specifications. Glycerol can be separated from biodiesel through gravity. If a heterogeneous catalyst is used, it can be removed from biodiesel by simple filtration or centrifugation. Removal of homogeneous catalyst, however, requires water and this step is called “biodiesel washing”. During the washing step, water is added to biodiesel, the mixture is shaken so that catalyst and alcohol are dissolved in the aqueous phase, and the water is then drained. This step is repeated until pH 7 of the washing water is obtained. In many cases, warm distilled water is used in order to avoid emulsion. The remaining moisture and alcohol are then evaporated. Sodium sulfate or silica gel may also be used for the removal of remaining water.

4. Biodiesel quality

The use of low-quality biodiesel due to incomplete reaction or contaminants in a diesel engine could result in several engine problems [7]. In order to protect consumers from unknowingly purchasing substandard fuel, several fuel standards have been adopted for quality control. Among these standards, ASTM D6751 (the American Society for Testing and Materials) [164] and EN 14214 (European Committee for Standardization) [165] are the most referred standards for pure biodiesel and are presented in Table 8. In addition, AOCS (American Oil Chemists' Society) has established official test methods for biodiesel quality and these methods are also listed in Table 8 [166]. It is reported that FAAE can be added at a low ratio to petroleum diesel fuel without substantially changing fuel properties [3]. The low-temperature flow property of the blended fuel with lower than 30% FAAE is not significantly changed from its parent petroleum diesel fuel. When FAAE that meets standard specifications is properly blended into petroleum diesel fuel and is handled according to standard techniques, the resulting fuel is of high quality and should perform well in a diesel engine. In the United States, ASTM D7467 is adopted for quality control of blended fuel containing 6–20% FAAE and is shown in Table 9 [167]. It is imperative that FAAE must meet standards for pure biodiesel prior to blending. Blends up to 5% are allowed in ASTM D957 for diesel fuel and ASTM D396 for heating oil provided that FAAE meets standards for pure biodiesel. In Canada, the Canadian General Standard Board has issued standard CAN/CGSB-3.520 for biodiesel-petroleum diesel blends up to 5% in 2005 which is shown in Table 9 [168]. The Canadian standard is intended for quality control of Type A-LS blends used in urban transit buses and passenger automobiles and Type B-LS blends used in engines in services involving relatively high loads as found in industrial and heavy mobile equipment, and the ASTM methods are adopted for testing the blended fuels.

4.1. Burning properties

The heating value of biodiesel and its parent oils is approximately 10% less than those of petroleum base diesel fuel on a mass basis [66,89,95]. However, higher viscosity of biodiesel reduces the

Table 8
Fuel standards and test methods for pure biodiesel.

Property	AOCS method	ASTM method	EN method	ASTM limits	EN limits
Acid value	Cd 3d-63	ASTM D664	EN14104	0.5 max[a] (mg KOH/g)[b]	0.5 max (mg KOH/g)
Water and sediment	Ca 2e-84	ASTM D2709	EN ISO 12937	0.05 max (vol%)	500 max (mg/kg)
Ester content	–	–	EN 14103	–	96.5 min (mol%)
MAG content	Cd 11b-91 Cd 11d-96	–	EN 14105	–	0.8 max (mol%)
DAG content	Cd 11b-91 Cd 11d-96	–	EN 14105	–	0.2 max (mol%)
TAG content	Ce 5–86 Ce 5b-89	–	EN 14105	–	0.2 max (mol%)
Free glycerol	Ca 14–56 Ca 14b-96	ASTM	EN 14105 EN 14106	0.02 (% mass)	0.02 max (mol%)
Total glycerol	Ca 14–56	ASTM	EN 14105	0.24 (% mass)	0.25 max (mol%)
Methanol	–	–	EN 14110	0.2 max (vol%)	0.2 max (mol%)
Ash content	Ca 11–55	ASTM D874	ISO 3987	0.02 max (% mass)	0.02 max (mol%)
Sulfur	Ca 8a-35	ASTM D5453	EN ISO 20846		10.0 max (mg/kg)
S15 grade	Ca 8b-35		EN ISO 20884	0.0015 max (% mass)	
S500 grade				0.05 max (% mass)	
Copper strip corrosion	–	ASTM D130	EN ISO 2160	No. 3 max	1.0 (degree of corrosion)
Phosphorous content	Ca 12–55 Ca 12b-92	ASTM D4951	EN 14107	0.001 max (% mass)	10.0 max (mg/kg)
Sodium and potassium, combined	Ca 15b-87	–	EN 14108 EN 14109	5.0 max (ppm)	5.0 max (mg/kg)
Calcium and magnesium, combined	Ca 15b-87	–	EN 14538	5.0 max (ppm)	5.0 mix (mg/kg)
Cetane number	–	ASTM D613	EN ISO 5165	47.0 min[a]	51.0 min
Iodine value	Cd 1–25	–	EN 14111	–	120 max (g I_2/100 g)
Linolenic acid content	–	–	EN 14103	–	12.0 max (mol%)
Polyunsatured ($\geq$ 4 double bonds) FAME	–	–	EN 14103	–	1.0 max (mol%)
Cloud point	Cc 6–25	ASTM D2500	–	–	–
Cold soak filterability	–	ASTM D7501	–	360 max (s)	–
Carbon residue	–	ASTM D4530	EN ISO 10370	0.05 max (% mass)	0.3 max; 10 % distillation residue (mol %)
Oxidation stability	Cd 12b-92	–	EN 14112	3.0 min (h)	6.0 min (h)
Flash point	Cc 9b-55	ASTM D93	EN ISO 3679	93 min (°C)	120 min (°C)
Density, 15 °C	Cc 10a-25	–	EN ISO 3675 EN ISO 12185	–	860–900 (kg/m^3)
Kinematic viscosity, 40 °C	–	ASTM D445	EN ISO 3104 ISO 3105	1.9–6.0 (mm^2/s)	3.5–5.0 (mm^2/s)
Distillation temperature, atmospheric equivalent, 90% recovered	–	ASTM D1160	–	360 max (°C)	–
Total contamination		–	EN 12662	–	24.0 max (mg/kg)

[a] For all tables: max refers to maximum and min refers to minimum.
[b] Units of the corresponding limits are displayed in parentheses.

amount of fuel that leaks past the plungers in the diesel fuel injection pump. In addition to heat of combustion, ignition delay time is also an important fuel burning characteristic. The ignition delay time is the time that passes between injection of fuel into the cylinder and onset of ignition and is characterized by cetane number (CN) [4]. A higher CN represents a shorter ignition delay time and vice versa. Cetane (hexadecane; $C_{16}H_{34}$) is a long straight-chain hydrocarbon and has been assigned a CN of 100. Most biodiesel from vegetable oils have CN higher than 51 and CN of specific ester such as that of stearic acid can be as high as 87 while the CN of petroleum base diesel usually ranges from 40 to 52 [169,170]. The higher CN of biodiesel stems from the fact that biodiesel is composed of linear chain molecules similar to that of cetane itself while petroleum base diesel is a mixture of hydrocarbons that typically contain 8–12 carbon atoms per molecule which comprises 75% saturated hydrocarbon including stretch, branched chains, and cycloalkanes and 25% aromatics. The branched chains, cycloalkanes and aromatics are responsible to the lower CN in petroleum base diesel. CN is usually characterized by ASTM D613. Alternatively since the CN of biodiesel increases with chain length and decreases with number of double bonds, CN of FAME can be estimated with reasonable accuracy using its saponification value and iodine value [171]. It is worthy to note that although CN of biodiesel increases with chain length, the use of longer chain alcohols such as ethanol or butanol as reacting alcohols in transesterification yields insignificant effect on CN of the resulting biodiesel [169].

4.2. Flow properties

Fuel flow property is an important characteristic as it determines the performance of a fuel flow system and can be evaluated by viscosity which measures the fluid's resistance to flow. A highly viscous fuel could lower the performance of the fuel flow system. One of the main reasons that the use of neat vegetable oil as diesel fuel has been considered to be unsatisfactory and impractical is because of its high viscosity [7]. In order to reduce its viscosity, the glycerol back bone of TAG is required to be stripped off usually by transesterification reaction. The resulting FAAE has been responsible for a significant reduction in viscosity compared to its parent oils. Due to the reduction of viscosity during transesterification, viscosity can also be used as means to monitor the extent of the transesterification reaction [162].

Since the viscosity of diesel fuels is a strong function of temperature and usually increases at lower temperatures, operating engines at cold climate regions is often challenging and

Table 9
Fuel standards ASTM D7467 for B6 to B20 and CAN/CGSB-3.520 for B1 to B5 blended biodiesel-petroleum diesel fuel.

Property	ASTM method	ASTM Limits	CGSB limits	
			Type A-LS[a]	Type B-LS[b]
Acid value	ASTM D664	0.3 max (mg KOH/g)	0.1 max (mg KOH/g)	0.1 max (mg KOH/g)
Water and sediment	ASTM D2709	0.05 max (vol%)	0.05 max (vol%)	0.05 max (vol%)
Ash content	ASTM D482	0.01 max (% mass)	0.01 max (% mass)	0.01 max (% mass)
Sulfur			500 max (mg/kg)	500 max (mg/kg)
S15 grade	ASTM D5453	15 max (μg/g)		
S500 grade	ASTM D2622	0.05 max (% mass)		
Copper corrosion, 3 h 50 °C	ASTM D130	No. 3 max	No. 1 max	No. 1 max
Cetane number	ASTM D613	40.0 min	40.0 min	40.0 min
One of the following must be met				
(1) Cetane index	ASTM D976	40.0 min	–	–
(2) Aromaticity	ASTM D1319	35.0 max (vol%)	–	–
Cloud point	ASTM D2500 ASTM D4539 ASTM D6371	–	–	–
Electrical conductivity at point, time and temperature of delivery to purchaser	ASTM D2624	–	25.0 min (pS/m)	25.0 min (pS/m)
Carbon residue, 10% bottoms	ASTM D524	0.35 max (% mass)	0.10 max (% mass)	0.16 max (% mass)
Oxidation stability	–	6.0 min (h)	–	–
Flash point	ASTM D93	52 min (°C)	40 min (°C)	40 min (°C)
Kinematic viscosity, 40 °C	ASTM D445	1.9–4.1 (mm^2/s)	1.3–3.6 (mm^2/s)	1.7–4.1 (mm^2/s)
Distillation temperature, atmospheric equivalent, 90% recovered	ASTM D86	343 max (°C)	290 max (°C)	360 max (°C)
Lubricity, HFRR 60 °C	ASTM D6079	520.0 max (μm)	–	–
Biodiesel content	ASTM D7371	6–20 (vol%)	–	–

[a] Type A-LS is intended for use in urban transit buses and passenger automobiles or when ambient temperatures require better low-temperature properties than Type B-LS.
[b] Type B-LS is intended for use in engines in services involving relatively high loads as found in industrial and heavy mobile equipment, such as intercity trucks and construction equipment, and when ambient temperatures and fuel storage conditions allow use of such fuel.

therefore the low temperature flow properties of fuel should be monitored closely. These properties can be examined by cloud point (CP), pour point (PP), and cold filter pligging point (CFPP). Cloud point is the temperature at which a cloud of wax crystals first appears in the oil when it is cooled and a cloudy fuel is visible to the naked eye. At temperatures below CP, crystals grow larger and agglomerate together to the point that they prevent the fluid to flow. The lowest temperature at which the fluid pours is defined as pour point. The CFPP is defined as the lowest temperature at which biodiesel flows under vacuum condition through a wire mesh filter screen within 60 s. In addition to CP, PP, and CFPP, a differential scanning calorimeter (DSC) has been used to evaluate low temperature properties of biodiesel [24,95,172]. At an adequately low temperature, a crystal is formed and the heat associated with crystallization is released and measured by DSC, and the temperature is recorded as onset crystallization temperature (OCT) which is the temperature at which the first crystal is formed. In addition to OCT, DSC is used to measure melting temperature, polymorphic transition temperature (temperature at which crystal changes its form), and the corresponding endothermic and exothermic heats.

The low temperature property of biodiesel is dependent mainly on its compositions. It is well known that unsaturated FAAE crystallizes at lower temperature than saturated FAAE due to its different three-dimensional configuration. Saturated molecules are in their minimum energy when fully extended and are well stacked, thereby strengthening the intermolecular attraction force [173]. Unlike saturated ester, especially *cis*-formation, unsaturated FAAE molecules have weaker intermolecular interactions and therefore crystallize at a lower temperature. The *tran*-formation fatty acids which usually occur unnaturally have similar molecular arrangement to those saturated fatty acids and therefore would crystallize at temperature higher than that of the corresponding *cis*-formation fatty acids. Branched molecules also have weak intermolecular force and therefore crystallize at low temperatures. Based on this knowledge, there have been attempts to improve low-temperature flow property of biodiesel by introducing branched structure to the originally straight-chain FAAE either by means of transesterification with branched alcohols [173] or isomerization reaction [174]. Alternatively, low temperature additives such as glyceryl ethers produced from etherification of glycerol with isobutylene or tert-butanol in the presence of solid acid catalysts such as sulfonated carbon and amberlyst-15 have been used to improve CP biodiesel [174–177]. In addition to fatty acid compositions, transesterification intermediates such as DAG and MAG if present in FAAE can greatly deteriorate low-temperature flow properties of biodiesel. The transesterification intermediates especially saturated MAG induce stronger intermolecular force mainly due to molecular stacking and hydroxyl moiety in their molecules and therefore raise biodiesel low temperature properties such as CP, PP, CPFF, and OCT. In addition, it was found that the presence of saturated MAG in biodiesel induces precipitation even at the temperatures higher than CP which cause problems with fuel filterability [178,179].

4.3. Stability

Biodiesel is susceptible to oxidation which leads to fuel degradation; therefore oxidation stability of biodiesel is crucially important as it determines resistance to chemical changes brought about by oxidation reaction. The oxidation of biodiesel is similar to those of lipid oxidations as discussed in Section 2.8. In addition to oxidation, polymerization occurs due to the presence of double bonds to form higher molecular weight products, in turn, raising the biodiesel's viscosity. Oxidation stability of biodiesel depends greatly on fatty acid compositions and degree of unsaturation. Saturated FAAE is more stable than unsaturated ones, while polyunsaturated FAAE is at least twice as reactive to auto-oxidation than monounsaturated FAAE [180,181]. For the same number of double bond per molecule, FAAE with a longer chain or higher molecular weight would be less prone to auto-oxidation due to the lower molar concentration of double bond [182]. As an

example of this phenomenon, ethyl ester has shown higher oxidation stability compared to that of methyl ester [66,97]. In addition to degree of unsaturation, the position at which double bonds are located in an unsaturated molecule is also an important parameter to determine oxidation stability of biodiesel. It is reported that η-3 fatty acids autoxidize faster than η-6 fatty acids [183].

Some metals can accelerate oxidation of biodiesel. It has been shown in the literature that elemental copper has strong catalytic effects on biodiesel oxidation [182] and peroxide value of biodiesel increases more rapidly when a copper strip is immersed in a glass container of biodiesel when compared to that when a steel strip is used [184]. In addition, biodiesel is prone to hydrolytic degradation in presence of water. The hydrolytic reaction is strongly influenced by the initial acid value of biodiesel due to the catalytic effects of free fatty acid on the reaction [185]. Biodiesel with high concentration of transesterification intermediates, i.e., DAG and MAG, has high tendency to absorb water, therefore promoting hydrolytic reaction. Most vegetable oils contain natural anti-oxidant reagents, i.e. tocopherol or Vitamin E, which hinder the oxidation reaction. Once the amount of anti-oxidants is depleted, the rate of oxidation increases rapidly. An addition of synthetic anti-oxidants such as tert-butyl hydroquinone (TBHQ), 3-tert-butyl-4-hydroxyanisole (BHA), pyrogallol (PY), and n-propyl gallate (PG) up to 1000 mg/kg may be required as these compounds have shown to improve the oxidation stability of biodiesel. The effects of another widely used anti-oxidant 2,6-di-tert-butyl-4-methyl-phenol (BHT) in food industry, is controversial when used to improve biodiesel stability [186,187]. Most biodiesel properties such as viscosity, density, CFPP, carbon residue are not affected by the addition of anti-oxidants. However, addition of high amounts of anti-oxidants can alter acid value of biodiesel [188].

Oxidation stability of biodiesel is preferably determined by the rancimat method as per EN 14112 or AOCS Cd 12b-92. During the Rancimat test, the biodiesel sample is heated to 110 °C and oxygen is supplied. In presence of oxygen at high temperature, the oxidation reaction takes place and the oxidation derivatives are transferred to the measuring chamber containing Millipore water. The increase in conductivity of water is detected as the oxidation derivatives are transferred into water. The induction time is defined as the time required for the conductivity of water to be increased rapidly and is used as an indication of biodiesel oxidation stability. Alternatively, oxidation stability of biodiesel can be evaluated by peroxide value (PV) and iodine value (IV). PV of biodiesel increases when FAAE oxidation initiates and propagates to form peroxides and hydroperoxides. However PV is not a very suitable parameter for determining oxidation stability because its value drops during further degradation of hydroperoxides to form secondary oxidation derivatives [184,189]. IV indicates degree of unsaturation in terms of mg Iodine per 100 g sample and is often used to correlate with oxidation stability of the test sample. The major flaw of this method as oxidation stability indicator is that it does not take into account the positions at which double bonds are located in a molecule, which has been proven to be a contributing factor for autoxidation of fatty acids [183]. Pressurized differential scanning calorimeter (PDSC) has also been used to determine oxidation stability of biodiesel. Since oxidation is an exothermic reaction, the reaction heat makes it possible to use DSC to monitor biodiesel oxidation process. Operating DSC at high pressure helps to increase the number of mole of oxygen available for the reaction, thereby accelerating oxidation to take place at lower temperature [190]. The results from the DSC method are in line with those obtained from the Rancimat method and it requires lesser amounts of sample and shorter analyzing time [191]. DSC was concluded to be a reliable alternative method to determine oxidation stability of biodiesel.

4.4. Lubricity

The lubricating property of fuel is defined as the quality that prevents wear when two moving metal parts come into contact with each other [192]. Oxygen and nitrogen containing compounds are responsible for the natural lubricating property of diesel fuel [193]. In petroleum refineries, processes such as hydrotreating are usually used to remove sulfur that also destroys heterocyclic oxygen and nitrogen containing compounds which are responsible for providing lubricity to the fuel [194]. Consequently, this typically ultra-low sulfur diesel fuel exhibits poor lubricity. ASTM D6079 is typically used to evaluate lubricating property of biodiesel and diesel fuel by the High-Frequency Reciprocating Rig (HFRR). In this method, the ball and disk are submerged in the test fluid and rubbed against each other for 75 min at 50 Hz to generate a wear. At the end of the test, the wear diameter was measured on the ball and the high wear diameter indicates poor lubricating property of the test fluid and vice versa. It was shown that the blended mustard biodiesel-petrodiesel samples have superior lubricating property as compared to those of commercial diesel fuels purchased from different gas stations (Esso, Shell, Petro-Canada, Co-op) [24]. This is explained by the presence of $COOCH_3$ moeity in methyl ester while the lower lubricating performance of esters prepared from higher alcohols is explained by an absence of $COOCH_3$ moeity. It was reported that the order of oxygenated moiety that provides lubricity is $COOH > OH > COOCH_3 > C{=}O > C–O–C$ [195].

Although biodiesel lubricating property is tested, compared with petroleum based diesel, and reported widely in the literature, tribological mechanism of biodiesel is still not available. Nevertheless, tribological mechanism of other model compounds such as zinc dialkyl-dithiophosphate (ZDDP) [196] may be useful in explaining the lubricity behavior of biodiesel. Initially, lubrication fluids are used to generate hydrostatic and hydrodynamic pressures to support the load. This condition is referred to as the elastohydrodynamic lubrication (EHL) regime where the fluid pressure is used to provide lubrication. Further increase in contact pressure causes thickness of the fluid film to decrease. When the average thickness of the fluid film falls below the average surface roughness, the boundary lubrication (BL) regime is applied. Under BL regime, the temperature is usually high enough to cause chemical reactions to take place between the lubricant and the solid surface, resulting in a chemical film that protects the surface. The reaction yields metallic-organo compounds which polymerize to form higher molecular weight products. These polymers (MW = 3000–5000) are critical in providing lubrication to the contacting surfaces. Petroleum diesel is a mixture of hydrocarbons that typically contains 8–12 carbon atoms per molecule with 75% saturated hydrocarbon and 25% aromatics. The reaction rate between petroleum diesel and the contacting surfaces in diesel engine is insufficient to form a film quickly enough. Unlike petroleum diesel, biodiesel contains a polar functional group such as $–COOCH_3$ in case of FAME in its molecule. This functional group promotes reactivity between biodiesel and metal surfaces forming a chemical film quickly enough to protect the surfaces. However, if the reaction rate is too rapid, chemical corrosion can occur causing an increase in wear.

The proposed chemical solution model of biodiesel blends in petroleum based diesel and involves aggregation of biodiesel molecules in reverse micelle formation (polar group in the inside and hydrocarbon tail on the outside) if the biodiesel concentration is high enough (see Fig. 10). Outside reverse micelle of FAAE lays free molecular region in which each molecular species compete freely for adsorption on the solid surface. When these free molecules are depleted, the reverse micelle dissociates release more free species. This model is used to explain how a lubricant

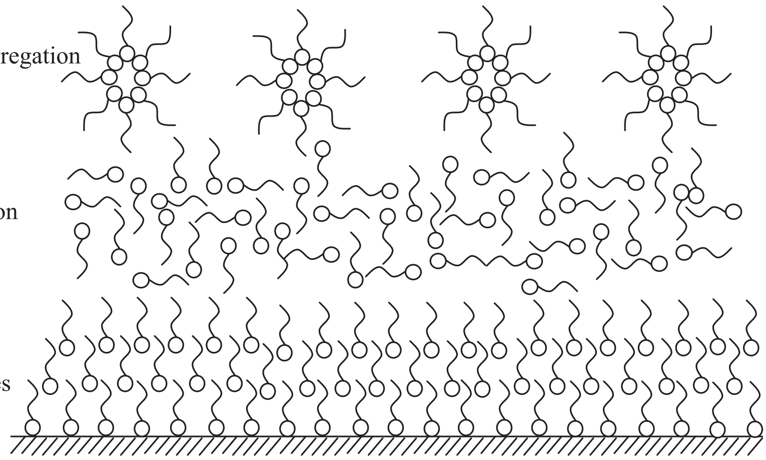


Fig. 10. Chemical solution model for biodiesel blends.

maintains its functionality throughout its lubricating life. In addition to polar head, the hydrocarbon chain has great impact on biodiesel lubricating properties. Hydrocarbon chain length, degree of branching, and the presence of double bond influence how the lubricant pack themselves on the solid surface resulting in the packing density. Low packing density film allows lubricating molecules to move about, hence providing flexibility and longevity to the lubricant. On the other hand, high packing density film has mechanical strength necessary for load-bearing ability. Increase in hydrocarbon chain length results in a lower packing density film which improves lubricating longevity but the load-bearing ability is decreased. In addition, an increase in alkyl chain length leads to reduction in molar concentration of the functional group resulting in a slower rate of the reaction between lubricant and the solid surface. However, if the chain length is insufficient, FAAE would lose its durability as a lubricant. A good lubricating biodiesel should be composed of varieties of FAAE to provide molecular mobility as well as solid adhesion strength.

4.5. Minor components

Minor components usually presented in vegetable oil are presented in Fig. 11. A comprehensive database of lipid classification including these minor components can be found in the literature [197]. These components affect biodiesel characteristics differently.

4.5.1. Pigments

Chlorophylls and their derivatives (see Fig. 12) have been reported for their detrimental effects on biodiesel stability [97] because they are effective photoreceptor. Chlorophyll is responsible for the green color in plants such as canola oil. In fact, if canola oil contains higher amounts of chlorophyll, the oil is downgraded, has lower economic value, and is labeled as greenseed canola oil [198]. Chlorophyll can generally be categorized into 2 types: Chlorophyll A (contains $-CH_3$ as its functional group) and Chlorophyll B (contains –CHO as its functional group). For plant growth, these two types of chlorophylls absorb sunlight at slightly different wavelength, thereby complimenting each other [199]. In addition, chlorophyll can degrade into various compounds depending on the surrounding conditions (see Fig. 12). In the presence of weak acids, magnesium ion is removed and chlorophyll degrades to pheophytin. Chlorophyllase, which is found mostly in plants such as ferns, mosses, and algae, can act as a catalyst for the removal of phytol tail from a chlorophyll molecule to form chlorophyllide. It is reported that chlorophyll derivatives could be converted to compounds that are capable of being prooxidants, thus having deleterious effect on the stability of vegetable oils [200]. In contrast, tocopherols such as α-tocopherol or vitamin E are present naturally in most vegetables and they are reported widely for their antioxidative activity [186,187,201,202].

In addition to chlorophylls, carotenoids are organic pigments that naturally occur in plants and can be categorized into two classes, xanthophylls (contain oxygen) and carotenes (purely hydrocarbons and contain no oxygen). The most common carotenoid in vegetable oils such as palm oil is β-carotene which is depicted in Fig. 12. β-Carotene is responsible for the red-orange color in plants and fruits and the color is darkened at elevated temperatures. Most carotenoids are known for their anti-oxidant activity as they are efficient free radical scavengers and therefore enhance the biodiesel oxidative stability [201,203]. However, they could interfere the biodiesel production process especially in homogeneous base catalyzed transesterification as the mechanism involves attack of alkoxide ion to the carbonyl carbon of the triglyceride molecule.

4.5.2. Lecithin and phospholipids

Lecithin is a mixture of various phospholipids that contain hydrophilic head and hydrophobic tails. Fig. 12 shows molecular structure of phospholipid possessing hydrophilic and hydrophobic property in its molecule. The hydrophilic head is negatively charged with a phosphate group and another possible polar group while the hydrophobic tails usually consist of fatty acid chains. Because phospholipids consist of both polar head and nonpolar tails, they act as co-solvents in transesterification enhancing vegetable oils' solubility in alcohols. However, phosphorous can be carried over from vegetable oils, i.e. phospholipid and can poison catalysts used for exhaust emissions.

4.5.3. Phytosterols

Phytosterols are referred to all sterols of plant origins. The chemical structure of sterols is composed of alkyl chain attached to sterol nucleus and is presented in Fig. 12. Most phytosterols contain 28–30 carbon atoms and 1–2 carbon-carbon double bonds (one in sterol nucleus and possibly one in the alkyl chain) in their molecule. It can be found as free sterol, acylated (sterol esters), alkylated (sterol alkyl ethers), sulfated (sterol sulfate), or linked to a glycoside moiety (sterol glycosides), and acylated sterol glycosides. During transesterification, acylated sterol glycosides are converted into sterol glycosides (SG) due to the alkaline catalysts. Therefore SG concentration in biodiesel is usually higher than that found in the vegetable oil feedstock. The chemical structure of an example of SG is depicted in Fig. 12. SG in biodiesel can accelerate

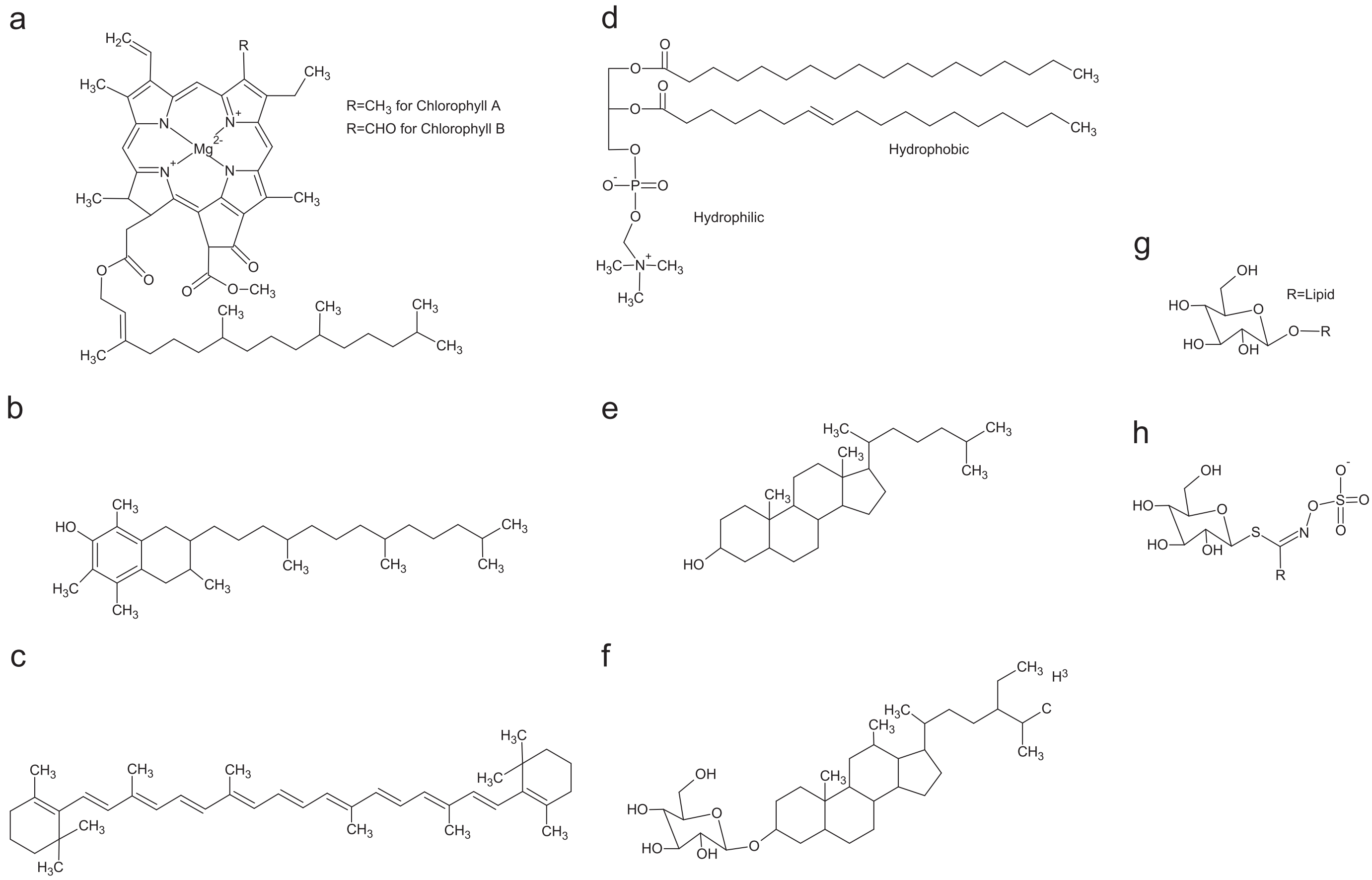


Fig. 11. Minor components in vegetable oils (a) chlorophyll, (b) α-tocopherol or vitamin E, (c) β-carotene, (d) phospholipid, (e) sterol, (f) sterol glycoside (β-sitosterol-β-D-glucopyranoside), (g) glycolipid and (h) glucosinolate.

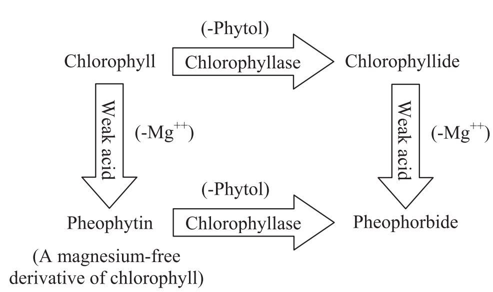


Fig. 12. Chlorophylls degradation pathways.

precipitate formation even above the biodiesel's cloud point and possibly block fuel filters due to its polarity and limited solubility. Among several sterols, SG has been found as the major component in biodiesel precipitates. Either GC or HPLC may be used to detect and quantify the presence of SG.

4.5.4. Glycolipids

Glycolipids are lipids with carbohydrates attached to them. Examples of glycolipids are sterol glycoside (SG) and glucosinolate as they are lipids attached to a carbohydrate. The chemical structure of glucosinolate is shown in Fig. 12. Glucosinolate is the major source of sulfur contained in biodiesel. Sulfur, like Phosphorus, is a potential catalyst poison and it is oxidized during combustion to produce SO_2 and SO_3 that in presence of water rapidly convert to sulfuric acid which leads to acid rain. Glucosinolates can be found in rapeseed oil while canola oil has low amounts of glucosinolates (see Section 2.2). Therefore, one can expect lesser amounts of sulfur content in biodiesel produced from canola oil compared to that derived from rapeseed oil.

5. Biodiesel production in Canada

Biodiesel production in Canada was below 50 million l per year in 2005. In December 2006, the federal government had announced an intention to mandate 2% renewable content in diesel fuel, which would create approximately 500 million l per year of biodiesel demand across the country. This announcement has served as a major driving force for tremendous growth in the Canadian biodiesel industry. The Canadian biodiesel production capacity had been increased to ~150 million l per year in 2008 and ~200 million l per year in 2010 [204]. The implementation date of the 2% federal mandate for biodiesel was later set on July 1, 2011 [205]. Prior to the federal mandate, there were a number of provincial renewable fuel mandates such as 2% in Alberta and Manitoba and 3% in British Columbia. The current major Canadian biodiesel plants using various feedstocks are listed in Table 10 indicating that the current total Canadian biodiesel production is 205.9 million l per year [204]. The feedstock for biodiesel production includes animal fats and waste vegetable oils (yellow grease) and only a small quantity of canola oil is used to produce biodiesel. A fraction of Canadian canola oil has been shipped to the United States for production of biodiesel, which is then shipped back to Canada to meet the mandate. In addition, Germany has been importing canola oil from Canada for their biodiesel production process and biodiesel usage. The Canadian biodiesel production industry is relatively new compared to that in the United States and many European countries since the first provincially

Table 10
Biodiesel plants in Canada.

Plant	Status	Feedstock	Capacity (million l per year)	City	Province
BioStreet Canada	Proposed plant	Oilseed	22	Vegreville	Alberta
Canadian bioenergy corporation – northern biodiesel limited partnership	Proposed plant	Canola	265	Lloyminster	Alberta
FAME biorefinery	Demonstration facility	Canola, camelina & mustard	1	Airdire	Alberta
Kyoto fuels corporation	Under construction	Multi-feedstock	66	Lethbridge	Alberta
Western biodiesel Inc.	Operational	Multi-feedstock	19	Calgary	Alberta
City-farm biofuel Ltd.	Operational	Recycled oil/tallow	10	Delta	British Columbia
Consolidated biofuels Ltd	Operational	Yellow grease	10.9	Delta	British Columbia
Bifrost bio-blends Ltd.	Operational	Canola	3	Arborg	Manitoba
Eastman bio-fuels Ltd.	Operational	Canola	5	Beausejour	Manitoba
Speedway international Inc.	Operational	Canola	20	Winnipeg	Manitoba
Bioversel Sarnia	Proposed plant	Multi-feedstock	170	Sarnia	Ontario
BIOX corporation	Operational	Multi-feedstock	66	Hamilton	Ontario
BIOX corporation (Plant 2)	Proposed plant	Multi-feedstock	67	Hamilton	Ontario
Methes energies Canada	Operational	Yellow grease	5	Mississauga	Ontario
Methes energies Canada	Under construction	Multi-feedstock	50	Sombra	Ontario
Noroxel energy Ltd.	Operational	Yellow grease	5	Springfield	Ontario
Biocardel Quebec Inc.	Proposed plant	Multi-feedstock	40	Richmond	Quebec
Bio-Lub Canada.com	Operational	Yellow grease	10	St-Alexis-des-Monts	Quebec
QFI biodiesel Inc.	Operational	Multi-feedstock	5	St-Jean-d'Iberville	Quebec
Rothsay biodiesel, a member of maple leaf foods Inc.	Operational	Multi-feedstock	45	Sainte-Catherine	Quebec
TRT-ETGO	Proposed plant	Vegetable oil	100	Bécancour	Quebec
Milligan Bio-Tech Inc.	Operational	Canola	1	Foam Lake	Saskatchewan

mandated market was established in 2009. The new Canadian 2% renewable fuel standard (RFS) requirement is anticipated to drive biodiesel production and market growth for sustainable future.

6. Conclusions

It is expected that biodiesel will be in high demand in the coming years as conventional diesel additives. The use of vegetable oils as feedstock will play a major role in supplying biodiesel to various sectors such as those of agriculture and transportation. The use of different vegetable oil affects production processes and costs as well as the resulting biodiesel characteristics. For example, used cooking oil requires pre-treatment prior to traditional alkali-catalyzed transesterification. Palm oil is selected in tropical countries due to its high oxidation stability but canola oil is a preferred choice in cold-climate countries due to its resistant to freeze at low temperature. Therefore, selection of vegetable oil and production technology is vital for growth in biodiesel industries. In order to make an effective decision, in-depth information and understandings on biodiesel from vegetable oils is essential.

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